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SODIUM FORMATE

[141-53-7]

Formula HCOOH; MW 68.008

Uses

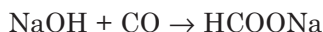
Sodium formate is used as a reducing agent, in dyeing and printing fabrics, in manufacturing formic and oxalic acids and sodium dithionite, as an analytical reagent for precipitating noble metals, and as a complexing agent. Sodium formate also is used as a buffering agent to adjust the pH of strong acids to higher values.

Physical Properties

White crystals; slightly hygroscopic; faint odor of formic acid; density 1.92 g/cm³; melts at 253°C; decomposes on further heating, first forming sodium oxalate and hydrogen and then sodium carbonate; very soluble in water; the aqueous solution neutral, pH about 7; soluble in glycerol; slightly soluble in alcohol; insoluble in ether.

Preparation

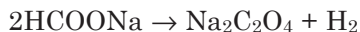
Sodium formate is prepared by heating sodium hydroxide with carbon monoxide under pressure:



Also, it is obtained as a byproduct from manufacturing pentaerythritol, C(CH₂OH)₄.

Analysis

Elemental composition: Na 33.81%, C 17.66%, H 1.48, O 47.05%. An aqueous solution may be analyzed to measure the sodium content of the salt. Reaction with noble metal in solution precipitates metal formate which can be filtered, dried and weighed to determine formate concentration. Also, an aqueous solution may be titrated against a standard solution of any suitable oxidizing agent. Another method is to decompose sodium formate to sodium oxalate above 253°C, cooling the mixture, dissolving with water and analyzing the aqueous solution for the oxalate ion by redox titration or ion chromatography, and analyzing sodium by AA or ICP method.



SODIUM HYDRIDE

[7646-69-7]

Formula NaH; MW 24.00

Uses

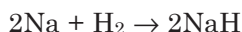
Sodium hydride is used as a reducing agent and reduction catalyst. It also reduces oxide scale on metals.

Physical Properties

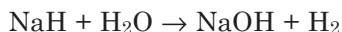
Silvery needles; refractive index 1.470; density 0.92 g/cm³; decomposes at 800°C; decomposes explosively in water; reacts violently with lower alcohols; dissolves in molten sodium and molten sodium hydroxide; insoluble in liquid ammonia, benzene, carbon tetrachloride and carbon disulfide.

Preparation

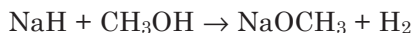
Sodium hydride is prepared by passing hydrogen gas into molten sodium metal dispersed in oil. Alternatively, the hydride can be made by passing hydrogen into sodium dispersed over the surface of an inert solid, such as, hydrocarbon above 200°C

**Reactions**

Sodium hydride is a powerful reducing agent. It reduces metal oxides, metal chlorides, and a number of oxidizable substances. Its reactions with water can proceed with explosive violence:



Also, its reactions with alcohols can be vigorous to violent. With lower alcohols the reaction is usually violent:

**Analysis**

Elemental composition: Na 95.79%, H 4.21%. The hydride is dissolved in water in small amounts (violent reaction occurs with water) very cautiously and the solution is analyzed for sodium. Another aliquot of solution is measured to determine concentration of OH⁻ (of the product NaOH) formed by acid-base titration.

SODIUM HYDROXIDE

[1310-73-2]

Formula: NaOH; MW 39.997

Synonyms: caustic soda; white caustic; sodium hydrate

Uses

Sodium hydroxide is one of the most important industrial chemicals. In vol-

ume, it is in the top ten chemicals produced in the United States. It is used in manufacturing a large number of compounds including several sodium salts, in treating cellulose for producing rayon and cellophane, and in manufacturing soaps, detergents, pulp, and paper. Sodium hydroxide is a common neutralizing agent for acids in acid-base titrations and petroleum refining. Another major application is extracting metals from their ores where alkali fusion, such as fusion with caustic soda, often is applied to open the ores. Additionally, sodium hydroxide is used to precipitate metals as hydroxides. Other uses are in reclaiming rubber, dissolving casein in plastics production, refining vegetable oils, processing textiles, as an eluant in ion chromatography, etching and electroplating, and as a laboratory reagent. Sodium hydroxide also is used as a strong base in many organic synthesis and base-catalyzed reactions.

Physical Properties

White orthorhombic crystals, produced in the form of pellets, lumps, sticks, beads, chips, flakes or solutions; hygroscopic; very corrosive; rapidly absorbs CO_2 and water from the air; density 2.13 g/cm^3 ; melts at 323°C ; vaporizes at 1388°C ; vapor pressure 1 torr at 739°C and 5 torr at 843°C ; very soluble in water (110 g/100mL at room temperature), generating heat on dissolution; aqueous solutions highly alkaline, pH of 0.5% solution about 13 and 0.05% solution about 12; soluble in methanol, ethanol and glycerol (23.8 g/100 mL methanol and 13.9 g/100 mL ethanol at ambient temperatures.)

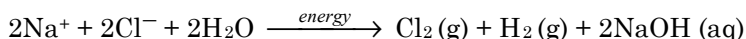
Thermochemical Properties

ΔH_f°	-101.7 kcal/mol
ΔG_f°	-90.7 kcal/mol
S°	15.4 cal/deg mol
C_p	14.2 cal/deg mol
ΔH_{fus}	1.58 kcal/mol
ΔH_{vap}	41.8 kcal/mol
ΔH_{soln}	-10.64 kcal/mol

Production

Sodium hydroxide is manufactured together with chlorine by electrolysis of sodium chloride solution. Various types of electrolytic cells are used commercially. They include the mercury cell, the diaphragm cell, and the membrane cell.

A saturated solution of brine is electrolyzed. Chlorine gas is liberated at the anode and sodium ion at the cathode. Decomposition of water produces hydrogen and hydroxide ions. The hydroxide ion combines with sodium ion forming NaOH. The overall electrolytic reactions may be represented as:

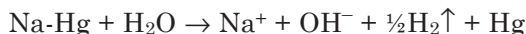


The mercury cell proceeds in two stages that occur separately in two cells. The first is known as the brine cell or the primary electrolyzer in which sodium ion

deposits on the mercury cathode forming amalgam, while chlorine gas is liberated at the anode:



In the second cell, known as the decomposer cell, a graphite cathode is used while sodium amalgam serves as the anode. Water reacts with the sodium metal of the amalgam in the decomposer:



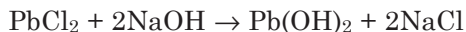
In chlor-alkali diaphragm cells, a diaphragm is employed to separate chlorine liberated at the anode from the sodium hydroxide and hydrogen generated at the cathode. Without a diaphragm, the sodium hydroxide formed will combine with chlorine to form sodium hypochlorite and chlorate. In many cells, asbestos diaphragms are used for such separation. Many types of diaphragm cells are available.

Sodium hydroxide is produced either as an anhydrous solid or as a 50% aqueous solution.

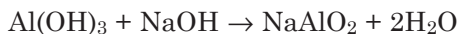
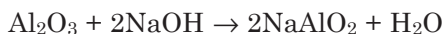
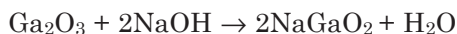
Reactions

Sodium hydroxide is a strong base. The most important reactions are the neutralization reactions with acids that form salts and water. Thus with sulfuric, hydrochloric, and nitric acids, the corresponding sodium salts are obtained when solutions are evaporated for crystallization. Neutralization with weak acids forms basic salts. Reactions with organic acids produce their soluble sodium salts.

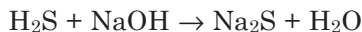
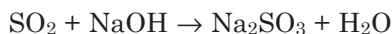
Another type of reaction is double decomposition producing metal hydroxides. Thus, insoluble heavy metal hydroxides may be precipitated by treating caustic soda with a soluble metal salt:

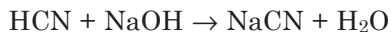


Reactions with the oxides and hydroxides of amphoteric metals form soluble sodium salts of metal oxides:

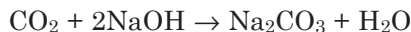


Sodium hydroxide reacts with weak acid gases to form salts:

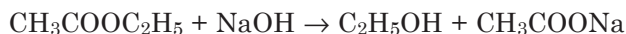




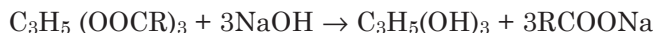
A similar reaction occurs with carbon dioxide forming sodium carbonate:



Saponification of esters with sodium hydroxide is an important commercial reaction. In general, the reaction involves an ester reacting with sodium hydroxide to form an alcohol and sodium salt of the organic acid; for example, ethyl acetate forming ethanol and sodium acetate:



or the formation of glycerol from fatty acid triglycerides:



Analysis

As a strong base, the strength of caustic soda solution can be determined by titration with a standard solution of strong acid using a color indicator or by potentiometric titration using a pH meter. Also, concentration of sodium in an aqueous solution can be measured by AA or ICP spectrophotometry.

Toxicity

Sodium hydroxide is highly corrosive to skin. Contact with eyes can damage vision.

SODIUM HYPOCHLORITE

[7681-52-9]

Formula NaClO ; MW 74.442; exists as a stable pentahydrate, $\text{NaClO} \cdot 5\text{H}_2\text{O}$

Synonym: sodium oxychloride

Uses

Sodium hypochlorite is marketed only as an aqueous solution because the anhydrous solid is highly unstable and can explode. The solid pentahydrate also is unstable in air, decomposed by reaction with carbon dioxide from air. Aqueous solutions are very stable. They are used for bleaching textiles and paper pulp; in cleaning solutions; in water purification; as a disinfectant for swimming pools; and as a germicide and topical antiinfective. The hypochlorite also is used as an oxidizing agent in many preparative reactions. It is an ingredient of commercial bleaching products such as Clorox and Dazzle.

Physical Properties

Anhydrous sodium hypochlorite explodes; the pentahydrate is a pale-green

crystalline solid; orthorhombic structure; density 1.6 g/cm³; melts at 18°C; decomposed by CO₂ in the air; soluble in water, 29.3 g/100 mL at 0°C; the aqueous solution is highly stable.

Preparation

Sodium hypochlorite solution is obtained by passing chlorine into sodium hydroxide solution. The pentahydrate is obtained by crystallization.

Analysis

The hypochlorite ion may be identified most distinctly by ion chromatography. Its concentration in the aqueous solution combined as ClO⁻ and molecular Cl₂ (which is partly formed when hypochlorite is dissolved in water) can be measured by iodometric titration. A measured volume of sodium hypochlorite solution is added to a small volume of an acidified solution of potassium iodide (in excess). Iodine liberated is titrated with a standard solution of sodium thiosulfate or phenyl arsine oxide using starch as indicator. Blue color of starch solution decolorizes at the end point.

Toxicity

Skin contact with the solid hypochlorite pentahydrate or its concentrated solution can cause irritation. Ingestion may cause corrosion of mucous membranes and gastric perforation.

SODIUM IODIDE

7681-82-5]

Formula: NaI; MW 149.89

Uses

Sodium iodide is an iodine supplement in food, an expectorant, cloud seed to cause rain, and solubilizes iodine in aqueous solution for analytical work. The radioactive iodide salt of sodium, Na(I-131) is used to diagnose thyroid function.

Physical Properties

White crystalline deliquescent powder or granules; saline and slight bitter taste; absorbs moisture from air; slowly turns brown on exposure to air due to iodine evolved; density 3.67g/cm³; melts at 660°C; vaporizes at 1,304°C; vapor pressure 1 torr at 767°C and 5 torr at 857°C; very soluble in water, 178.7 g/100 mL at 20°C and 294 g/100 mL at 70°C; soluble in ethanol and acetone.

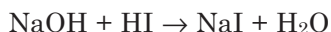
Thermochemical Properties

ΔH_f°	-68.79 kcal/mol
ΔG_f°	-68.38 kcal/mol

S°	23.54 cal/deg mol
C_p	12.45 cal/deg mol

Preparation

Sodium iodide is prepared by adding hydriodic acid or an acidic iodide solution to a solution of sodium hydroxide or sodium carbonate, followed by evaporation and crystallization:



The solution is filtered to remove any impurities prior to its evaporation and crystallization.

Analysis

Elemental composition: Na 15.34%, I 84.66%. Aqueous solution is analyzed for sodium by AA or ICP and for iodide ion by ion chromatography or leukocrystal violet colorimetry (See Iodine). Alternatively, in an acidified solution of sodium hypochlorite, a measured amount of sodium iodide is titrated against a standard solution of sodium thiosulfate or phenyl arsine oxide using starch indicator to detect the end point.

SODIUM NITRATE

[7631-99-4]

Formula: NaNO_3 ; MW 84.99

Synonyms: Chile saltpeter; Chilean nitrate; soda niter

Occurrence and Uses

There are several natural deposits of sodium nitrate in various parts of the world, including Chile, Mexico, Egypt, and the United States. The most important application of sodium nitrate is its use as a fertilizer in agriculture. It is an effective fertilizer for cotton, tobacco, and vegetable crops. Its agricultural applications, however, have dwindled considerably in recent years because of the growth of ammonium nitrate and other fertilizers.

Another major use of sodium nitrate is in manufacturing explosives. It is a component of many types of dynamites and water-based slurry type blasting explosives. Sodium nitrate also is used in making charcoal briquettes. Sodium nitrate is used as an oxidizing and fluxing agent in manufacturing vitreous glass, fiberglass, porcelain, and enamels. Other uses are in the heat-treatment baths for alloys and metals, as a food preservative, in curing meats, and in preparing various salts.

Physical Properties

Colorless crystalline solid; saline taste; trigonal, and rhombohedrals structure; density 2.257g/cm³; refractive index 1.587 (trigonal) and 1.336 (rhombo-

hedral); melts at 308°C; decomposes at 380°C; specific conductance 95 $\mu\text{mhos/cm}$ at 300°C; viscosity 2.85 centipoise at 317°C; very soluble in water 92.1 g/100 mL at 25°C and 180 g/100 mL at 100°C; very soluble in liquid ammonia; soluble in alcohol.

Thermochemical Properties

ΔH_f°	-111.82 kcal/mol
ΔG_f°	-87.73 kcal/mol
S°	27.85 cal/deg mol
C_p	22.20 cal/deg mol
ΔH_{fus}	3.585 kcal/mol

Production

Sodium nitrate is recovered from natural deposits. One such process, known as the Guggenheim nitrate process, is briefly outlined below: The ore is crushed. Sodium nitrate is leached from the ore by extraction with a brine solution at 40°C. The brine for leaching is made up of an aqueous solution of magnesium sulfate, MgSO_4 , and calcium sulfate, CaSO_4 . The caliche variety of Chilean ore contains mostly sodium nitrate and sodium chloride as the main saline components, along with limestone, clays, sand, lime, and inert volcanic rocks. Sodium nitrate usually occurs in this ore as a double salt with sodium sulfate $\text{NaNO}_3 \cdot \text{Na}_2\text{SO}_4 \cdot \text{H}_2\text{O}$. This double salt, which is sparingly soluble in water, is broken down by magnesium in leaching brine solution, thus releasing more sodium nitrate into the extract. Sodium nitrate finally is recovered from the leachate brine by fractional crystallization.

Brines of other compositions have been used to extract sodium nitrate from its ores. Many such processes, including the Shanks process practiced in the past to produce sodium nitrate, are now obsolete.

Analysis

Elemental composition: Na 27.08%, N 16.48%, O 56.47%. An aqueous solution of the salt is analyzed for sodium by various instrumental techniques (See Sodium). Nitrate ion in solution can readily be measured by ion chromatography, nitrate-ion selective electrode, or various colorimetric methods, such as its reduction with cadmium to nitrite followed by diazotization.

SODIUM OXALATE

[62-76-0]

Formula $\text{Na}_2\text{C}_2\text{O}_4$; MW 134.00

Synonym: ethanedioic acid disodium salt

Uses

Sodium oxalate is used as an analytical standard for standardization of potassium permanganate and other strong oxidizing agents. It also is used in finishing textiles, tanning leather, and blue printing.

Physical Properties

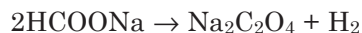
White crystalline powder; density 2.34 g/cm³; decomposes around 250° C; sparingly soluble in water, 3.7 g/100 mL at room temperature; moderately soluble in boiling water, about 6.25 g/100 mL; the aqueous solution is practically neutral; insoluble in alcohol

Thermochemical Properties

$$\Delta H_f^\circ \text{ (gas)} \quad -315.0 \text{ kcal/mol}$$

Preparation

Sodium oxalate can be made by heating sodium formate at about 250°C:



It also can be prepared by reacting oxalic acid with a dilute aqueous solution of sodium hydroxide followed by evaporation and crystallization.

Analysis

Elemental composition: Na 34.32%, C 17.92%, O 47.76%. The aqueous solution is analyzed for sodium by AA or ICP method. The oxalate ion is quantitatively determined by titration against a standard solution of potassium permanganate.

SODIUM PHOSPHATE, DIBASIC

[7558-79-4]

Formula: Na₂HPO₄; MW 141.96; forms a dihydrate, Na₂HPO₄•2H₂O, heptahydrate, Na₂HPO₄•7H₂O and a dodecahydrate, Na₂HPO₄•12H₂O.

Synonyms: sodium hydrogen phosphate; disodium hydrogen phosphate; dibasic sodium phosphate; disodium phosphate; disodium orthophosphate; and sodium orthophosphate, secondary. The dihydrate is known as Sorensen's phosphate.

Uses

The dibasic salt is used as a laboratory reagent and a buffer in chemical analysis. Other uses are in manufacturing ceramics, detergents, and enamels; as a mordant in dyeing; for fireproofing paper and wood; for weighting and printing silk; in the treatment of boiler water; as a sequestrant in food; as a dietary supplement; in soldering enamels; and in fertilizers. It is used therapeutically as a cathartic.

Physical Properties

The anhydrous compound is white crystalline powder; hygroscopic; density 1.70 g/cm³; converts to sodium pyrophosphate at 240°C; soluble in water;

insoluble in alcohol.

The dihydrate is a crystalline powder or granular solid; density 2.066 g/cm³ at 15°C; loses water of crystallization at 92.5°C.

The heptahydrate is a powdered or granular crystalline solid; density 1.679 g/cm³; loses five molecules of water at 48°C.

The dodecahydrate is made up of translucent crystals or granules; density 1.524 g/cm³; readily loses five water molecules on exposure to air at ambient temperature; melts at 35°C when the salt contains all water of crystallization; loses all water at 100°C.

All the hydrates are soluble in water and insoluble in alcohol.

Thermochemical Properties

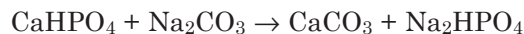
ΔH_f°	-417.8 kcal/mol
ΔG_f°	-384.4 kcal/mol
S°	36.97 cal/deg mol
C_p	32.34 cal/deg mol

Preparation

Dibasic sodium phosphate is prepared by treating phosphoric acid with a slight excess of sodium carbonate. The solution is boiled to expel carbon dioxide. Upon cooling dodecahydrate crystallizes out. Heating dodecahydrate at 100°C forms the anhydrous salt.



Dibasic sodium phosphate also is prepared by reacting dibasic calcium phosphate with sodium carbonate. The product calcium carbonate precipitates leaving dibasic sodium salt in the solution. The solution on cooling yields crystals of hydrated product.



Analysis

Elemental composition (anhydrous salt): Na 32.39%, P 21.82%, H 0.71%, O 45.08%. An aqueous solution may be analyzed to determine the sodium content. Phosphorus may be analyzed by various colorimetric methods (See Phosphorus).

SODIUM PHOSPHATE, MONOBASIC

[7558-80-7]

Formula NaH_2PO_4 ; MW 119.98; forms a monohydrate, $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$, [10049-21-5], MW 137.99; and a dihydrate, $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ [13472-35-0], MW 156.01.

Synonyms: sodium dihydrogen phosphate; sodium orthophosphate, primary; primary sodium phosphate; sodium biphosphate; monobasic sodium phosphate

Uses

Monobasic sodium phosphate is used in baking powders, acid cleansers, electroplating, as a dry acidulant, and in treating boiler water. It also is a nutrient supplement in food. It is a laboratory reagent used as a buffer.

Physical Properties

Anhydrous salt: white crystalline powder; slightly hygroscopic; forms sodium acid pyrophosphate, $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ on heating above 225°C and sodium metaphosphate $(\text{NaPO}_3)_n$ at about 350 to 400°C ; very soluble in water, aqueous solution acidic.

Monohydrate: white orthorhombic crystals or granules; density 2.04 g/cm^3 ; loses its water of crystallization at 100°C ; very soluble in water, pH of 1% solution 4.5; insoluble in alcohol.

Dihydrate: large transparent crystals; orthorhombic bisphenoidal structure; density 1.915 g/cm^3 ; decomposes at 60°C ; very soluble in water; insoluble in alcohol.

Preparation

Monobasic sodium phosphate can be prepared by partial neutralization of phosphoric acid with sodium hydroxide in equimolar amounts:



It also can be made by treating disodium hydrogen phosphate with phosphoric acid in proper stoichiometric amount:



Analysis

Elemental composition: Na 19.16%, P 25.81%, H 1.68%, O 53.34%. The compound is dissolved in water and analyzed by AA or ICP to determine its sodium content. The phosphorus is analyzed as total P by acid digestion and colorimetric method (See Phosphorus and also Phosphoric Acid).

SODIUM PHOSPHATE, TRIBASIC

[7601-54-9]

Formula: Na_3PO_4 ; MW 163.94; forms a stable dodecahydrate, $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ [7601-54-9], MW 380.12

Synonyms: trisodium phosphate; tertiary sodium phosphate; trisodium orthophosphate; tribasic sodium phosphate

Uses

Trisodium phosphate is used in detergents; in industrial cleaning solutions; in metal cleaner formulations; as a water softener; for the treatment of boiler water; as a paint remover; in photographic developers; for tanning leather; for manufacturing paper; in laundering; for clarifying sugar; as a dietary supplement; and a food additive. Also, it is a common laboratory reagent.

Physical Properties

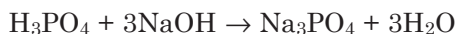
The dodecahydrate is a white or colorless hexagonal crystal; density 1.62 g/cm³; melts around 75°C on rapid heating; partially loses water of crystallization at 100°C; retains the last water molecule even at moderate ignition; soluble in water, about 28 g/100 mL at 20°C; the solution is strongly alkaline; the pH of a 0.1M solution 11.5; insoluble in alcohol.

Preparation

Trisodium phosphate may be prepared in two steps, first by adding a little excess of sodium carbonate to phosphoric acid and then boiling the solution to expel carbon dioxide. Sodium hydroxide is then added to the solution:



Alternatively, trisodium phosphate may be prepared by complete neutralization of phosphoric acid with sodium hydroxide, followed by evaporation and crystallization:



Analysis

Sodium is analyzed in aqueous solution by AA or ICP methods. Phosphate anion is measured by colorimetric methods (See Phosphoric Acid) or ion chromatography. The solution must be diluted appropriately. The compound is also identified from its physical properties.

SODIUM SULFATE

[7757-82-6]

Formula Na₂SO₄; MW 142.04; forms a decahydrate, Na₂CO₃•10H₂O (Glauber's salt) [7727-73-3]

Occurrence and Uses

Sodium sulfate occurs in nature as the minerals mirabilite and thenardite. While thenardite is the anhydrous form of Na₂SO₄, mirabilite is a naturally-occurring decahydrate, Na₂SO₄•10H₂O.

Sodium sulfate is one of the most important sodium salts. The decahydrate,

commonly known as the Glauber's salt, was first prepared by Johann Glauber in the seventeenth century as a by-product in making hydrochloric acid from sulfuric acid and sodium chloride.

Sodium sulfate is used in manufacturing paper pulp by the Kraft Process. Other uses are in manufacturing glass and ultramarine; in dyeing and printing textiles; as a filler in synthetic detergents; and for standardizing dyes. A major use of anhydrous sodium sulfate is as an agent to remove water from organic solvents and their extracts for organic synthesis and instrumental analysis. Sodium sulfate is a common laboratory reagent. Also, it is used to prepare other sodium salts.

Physical Properties

Anhydrous sodium sulfate is a white crystalline powder; orthorhombic or hexagonal structure; hygroscopic; refractive index 1.468; hardness 2.8 Mohs; density 2.664 g/cm³; melts at 884°C; soluble in water, insoluble in ethanol.

The decahydrate consists of colorless monoclinic crystals; refractive index 1.394; hardness 1.8 Mohs; density 1.46 g/cm³; decomposes at 32°C; soluble in water; insoluble in ethanol.

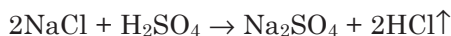
Thermochemical Properties

ΔH_f°	-331.5 kcal/mol
ΔG_f°	-303.6 kcal/mol
S°	35.76 cal/deg mol
C_p	30.64 cal/deg mol
ΔH_{fus}	5.64 kcal/mol

Production

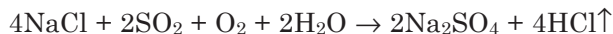
Sodium sulfate is mined from its natural mineral deposits and subjected to purification.

Sodium sulfate is synthesized by the Mannheim process or Hargreaves process. Mannheim's process is based on Glauber's reaction between sulfuric acid and sodium chloride:



The process was devised by Johann Glauber to produce hydrochloric acid. Sodium sulfate is isolated from the solution by fractional crystallization.

Hargreaves' process also was developed to produce hydrochloric acid. It is a variation of Mannheim's method. In this method, sulfur dioxide is used instead of sulfuric acid. The reaction is as follows:



Sodium sulfate also is obtained as a byproduct of manufacturing phenol by caustic fusion.

Analysis

Elemental composition: Na 32.38%, S 22.57%, O 45.06%. An aqueous solu-

tion may be analyzed to measure sodium content (See Sodium). Sulfate may be analyzed by gravimetry following precipitation with barium chloride solution as barium sulfate. Sulfate may be directly measured in the aqueous solution by ion chromatography. Water of crystallization in Glauber's salt can be measured by gravimetric analysis. Solid crystalline sodium sulfate can be identified by physical properties (i.e. refractive index) and x-ray properties.

SODIUM SULFIDE

[1313-82-2]

Formula Na_2S ; MW 78.046; forms a pentahydrate, $\text{Na}_2\text{S} \cdot 5\text{H}_2\text{O}$ [1313-83-3], MW 168.12 and a nonahydrate, $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ [1313-84-4], MW 240.18

Synonym: sodium monosulfide

Uses

Sodium sulfide is used in making sulfur dyes; for dehairing of hides; removing sulfur from viscous rayon; engraving and lithography; cotton printing; manufacturing rubber; paper pulp; and as a photographic reagent. Other major applications are for treating paper and for extracting gold ores where oxidized metal ores are converted to sulfides prior to froth flotation. Sodium sulfide also is used in preparing many other sulfides and as an analytical reagent.

Physical Properties

White cubic crystal; hygroscopic; density 1.856 g/cm³; melts at 1,172°C; soluble in water 18.6 g/100mL at 20°C and 39 g/100mL at 50°C; aqueous solutions strongly alkaline; slightly soluble in alcohol; insoluble in ether.

The pentahydrate consists of flat, shiny prismatic crystals; density 1.58 g/cm³; loses three water molecules at 100°C; melts at 120°C losing all water molecules; soluble in water and alcohol; aqueous solutions strongly alkaline; insoluble in ether.

The nonahydrate is a yellowish-white crystalline solid; tetragonal crystals; odor of hydrogen sulfide; the color changes on exposure to light and air, first turning to yellow and then becoming brownish-black, deliquescent; density 1.43 g/cm³; decomposes at about 50°C; very soluble in water; aqueous solution strongly alkaline; slightly soluble in alcohol; insoluble in ether.

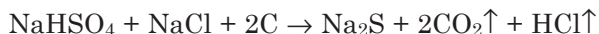
Thermochemical Properties

ΔH_f°	-87.19 kcal/mol
ΔG_f°	-83.60 kcal/mol
S°	20.00 cal/deg mol
ΔH_{fus}	4.54 kcal/mol

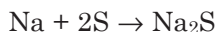
Preparation

Sodium sulfide is prepared by heating sodium bisulfate with sodium chlo-

ride and coal above 950°C. The product mixture is extracted with water and the hydrated sulfide is obtained from the solution by crystallization:

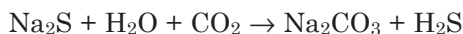


Sodium sulfide also is produced from its elements in liquid ammonia:



Reactions

Sodium sulfide in solid form reacts with carbon dioxide in the presence of moisture to form hydrogen sulfide and sodium carbonate. Thus, the H₂S odor of sodium sulfide crystals is attributed to its exposure to moist air:



In aqueous solution, sodium sulfide reacts with a number of metal salts forming insoluble sulfides.

When added to dilute mineral acids, hydrogen sulfide is generated.

Analysis

Elemental composition: Na 58.93%, S 41.07%. An aqueous solution is analyzed to determine sodium content. Also, an aqueous solution may be analyzed for sulfide by methylene blue colorimetric test or by iodometric titration (APHA, AWWA, and WEF. 1999. *Standard methods for the Examination of Water and Wastewater*, 20th ed. Washington, DC: American Public Health Association). The methylene blue test is based on reacting sulfide, ferric chloride and dimethyl-*p*-phenylenediamine to produce methylene blue. Also, sulfide can be measured by using a silver-silver sulfide electrode. Qualitatively, sulfide may be identified from the liberation of H₂S on treatment with acid. The H₂S turns the color of paper soaked with lead acetate black (See Hydrogen Sulfide).

SODIUM THIOCYANATE

[540-72-7]

Formula NaSCN; MW 81.074

Synonyms: sodium sulfocyanate; sodium sulfocyanide; sodium rhodanide; sodium rhodanate

Uses

Sodium thiocyanate is an analytical reagent for measuring iodide. Other uses are dyeing and printing textiles, preparing thiocyanate salts, and nickel plating.

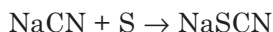
Physical Properties

Colorless crystals or white powder; deliquescent; melts at 287°C; very sol-

uble in water; soluble in alcohol.

Preparation

Sodium thiocyanate is prepared by boiling an aqueous solution of sodium cyanide with sulfur:



Analysis

Elemental composition: Na 28.36%, S 39.54%, C 14.81%, N 17.28%. The aqueous solution may be analyzed for sodium. Thiocyanate may be measured by gravimetry by reacting with ferric ion to form red ferric thiocyanate, $\text{Fe}(\text{SCN})_3$, which may be filtered, washed, dried, and weighed.

SODIUM THIOSULFATE

[7772-98-7]

Formula $\text{Na}_2\text{S}_2\text{O}_3$; MW 158.13; forms a stable pentahydrate, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ [10102-17-7], MW 248.19

Synonyms: sodium hyposulfite; hypo; antichlor

Uses

Sodium thiosulfate is a common analytical reagent used in iodometric titration to analyze chlorine, bromine, and sulfide. Other uses are in bleaching paper pulp, bleaching straw, ivory, and bones, for removing chlorine from solutions, silver extraction from its ores, a mordant in dyeing and printing textiles, and as an antidote to cyanide poisoning.

Another major application is in photography, where it is used as a fixer to dissolve unchanged silver salts from exposed negatives.

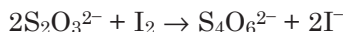
Physical Properties

Anhydrous thiosulfate is a white powder; soluble in water; insoluble in ethanol.

Sodium pentahydrate is a colorless, odorless, crystalline solid; density 1.69 g/cm^3 ; decomposes around 50°C ; effloresces in dry air above 33°C ; very soluble in water and oil of turpentine; insoluble in ethanol.

Preparation

Sodium thiosulfate is a common reducing agent. It reduces iodine to iodide anion forming sodium tetrathionate. This reaction is utilized in the so-called iodometric titration:



Sodium thiosulfate reacts with chlorine to form sodium bisulfate and hydrochloric acid. This reaction removes chlorine from aqueous solutions:



Sodium thiosulfate reacts with hydrochloric acid, decomposing to sulfur and sulfur dioxide:



Analysis

Elemental composition: Concentration of sodium thiosulfate in aqueous solution can be measured by titration with a standard solution of potassium iodate, potassium biiodate, or potassium dichromate using starch indicator. The oxidant is added to an acidified solution of excess potassium iodide before titrating with the thiosulfate solution.

STRONTIUM

[7440-24-6]

Symbol Sr; atomic number 38; atomic weight 87.621; a Group II A (Group 2) alkaline earth metal positioned between calcium and barium in its group; electron configuration $[\text{Kr}]5s^2$; valence state +2; atomic radius 2.15Å; ionic radius, Sr^{2+} 1.26Å and 1.44Å for coordination numbers 8 and 12 in crystals; standard electrode potential, E° for $\text{Sr}^{2+} + 2e^- \leftrightarrow \text{Sr}$ is -2.899V ; four stable natural isotopes: Sr-84(0.56%), Sr-86(9.86%), Sr-87(7.00%), Sr-88(82.58%); twenty-three artificial radioactive isotopes in the mass range 76-83, 85, 89-102; the longest-lived radioisotope is the beta emitter Sr-90, $t_{1/2}$ 29.1 year; the shortest-lived isotope is the beta-emitter Sr-102, $t_{1/2}$ 68ms.

History, Occurrence, and Uses

William Cruickshank in 1787 and Adair Crawford in 1790 independently detected strontium in the mineral strontianite, small quantities of which are associated with calcium and barium minerals. They determined that the strontianite was an entirely new mineral and was different from baryta and other barium minerals known at the time. In 1808, Sir Humphry Davy isolated strontium by electrolysis of a mixture of moist strontium hydroxide or chloride with mercuric oxide, using a mercury cathode. The element was named after the town Strontian in Scotland where the mineral strontianite was found.

Strontium is found in small quantities in many rocks and soils, mostly associated with calcium and barium. Its abundance in the earth's crust is about 370 mg/kg, about the same as barium. The average concentration of this metal in sea water is about 7.9 mg/L.

The two principal strontium minerals are its carbonate, strontianite, SrCO_3 , and the more abundant sulfate mineral celestite, SrSO_4 .

Elemental strontium has only minor uses, since most applications involve

calcium and barium. Strontium alloys are used as “getters” for vacuum tubes. It is incorporated in glass for making picture tubes for color television. Strontium compounds are used in tracer bullets and in fireworks to produce red signal flares. Strontium titanate is a gemstone. The radioactive strontium-90 with a half-life of 29 years is a high-energy beta emitter. It is a product of nuclear fission. This isotope is a lightweight nuclear-electric power source in space vehicles and remote weather stations.

Physical Properties

Silvery-white metal when freshly cut; rapidly turns yellow on exposure to air forming a thin oxide coating; face-centered cubic structure; malleable, ductile, and somewhat softer than calcium; density 2.64 g/cm³; melts at 777°C; vaporizes at 1,382°C; vapor pressure 5 torr at 847°C and 20 torr at 953°C; electrical resistivity 23 microhm-cm at 20°C; thermal neutron absorption cross section 1.21 barns; reacts with water; soluble in ethanol.

Thermochemical Properties

$\Delta H_f^\circ(\text{cry})$	0.0
$\Delta H_f^\circ(\text{gas})$	39.3 kcal/mol
$\Delta G_f^\circ(\text{gas})$	31.3 kcal/mol
$S^\circ(\text{cry})$	12.5 cal/deg mol
$S^\circ(\text{gas})$	39.3 cal/deg mol
$C_p(\text{cry})$	6.31 cal/deg mol
$C_p(\text{gas})$	4.97 cal/deg mol
ΔH_{fus}	1.78 kcal/mol
Thermal conductivity (at 27°C)	0.353 W/cm K
Coefficient of linear expansion (at 25°C)	$22.5 \times 10^{-6}/^\circ\text{C}$

Production

Strontium and its compounds are mostly derived from celestite, SrSO₄. The mineral is converted to its carbonate by heating with sodium carbonate. Alternatively, the mineral may be reduced to sulfide by heating with coke. The carbonate or the sulfide is then converted to other strontium salts.

Metallic strontium is produced by electrolysis of a mixed melt of strontium chloride and potassium chloride in a graphite crucible using an iron rod as cathode. The upper cathodic space is cooled and the strontium metal collects over the cooled cathode and forms a stick.

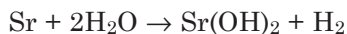
Strontium metal also can be prepared by thermal reduction of its oxide with aluminum. Strontium oxide-aluminum mixture is heated at high temperature in vacuum. Strontium is collected by distillation in vacuum. Strontium also is obtained by reduction of its amalgam, hydride, and other salts. The amalgam is heated and the mercury is separated by distillation. If hydride is used, it is heated at 1,000°C in vacuum for decomposition and removal of hydrogen. Such thermal reductions yield high-purity metal.

Reactions

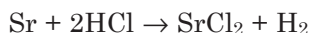
Strontium is a reactive metal, similar to calcium. Exposure to air forms strontium oxide, SrO. In finely-divided form, the metal is pyrophoric. It

ignites in air to form both the oxide, SrO, and the peroxide, SrO₂. Similarly, when heated with chlorine gas or bromine vapor, it burns brightly, forming its halides, SrCl₂ or SrBr₂. When heated with sulfur, strontium forms sulfide, SrS.

Strontium reacts vigorously with water forming the hydroxide, Sr(OH)₂, with liberation of hydrogen:



Sr metal reacts with acids evolving hydrogen and forming corresponding salts:



When heated under hydrogen it forms an ionic hydride, SrH₂, a stable crystalline salt. Heating Sr metal in a stream of nitrogen above 380°C forms nitride, Sr₃N₂.

Strontium also is a reducing agent. It reduces oxides and halides of metals at elevated temperatures to metallic form.

Analysis

Strontium and all its compounds impart crimson red color in the flame test. The metal in trace concentrations can be analyzed by various instrumental methods that include flame-and furnace-AA, ICP-AES, ICP/MS, x-ray fluorescence, and neutron activation analysis.

Hazard

The finely-powdered metal is pyrophoric. Its radioactive isotopes Sr-89 and Sr-90 emit high-energy beta radiation. They are extremely hazardous because they deposit in bones replacing calcium. Their radiation can damage bone marrow and blood-forming organs, inducing cancer.

STRONTIUM CARBONATE

[1633-05-2]

Formula: SrCO₃; MW 147.63

Occurrence and Uses

Strontium carbonate occurs in nature as mineral strontianite. The compound is used in pyrotechnics and ceramic ferrites. It also is used in making iridescent glass for color television tubes. Other uses are in refining sugar and preparing other strontium salts.

Physical Properties

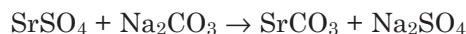
White orthorhombic crystals; refractive index 1.518; hygroscopic; hardness 3.5 Mohs; density 3.5 g/cm³; insoluble in water; soluble in dilute acids with liberation of carbon dioxide.

Thermochemical Properties

ΔH_f°	-291.6 kcal/mol
ΔG_f°	-272.5 kcal/mol
S°	23.2 cal/deg mol
C_p	19.5 cal/deg mol

Production

Strontium carbonate occurs in nature as strontianite and can be mined from its deposit. It is, however, usually made from the mineral celestite. Celestite is fused with sodium carbonate at elevated temperatures or boiled with a solution of ammonium carbonate:



Strontium carbonate is insoluble in water. It precipitates from the product mixture in the second reaction. If fused with sodium carbonate, the product mixture is leached with water. Insoluble carbonate separates from the water-soluble sodium sulfate.

Analysis

Elemental composition: Sr 59.35%, C 8.14%, O 32.51%. SrCO_3 is dissolved in dilute acid and carbon dioxide liberated is identified by the lime-water test (turns lime water milky). Strontium in solution is analyzed by various methods mentioned earlier (See Strontium).

STRONTIUM CHLORIDE

[10476-85-4]

Formula: SrCl_2 ; MW 158.53; forms a dihydrate, $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$ and a hexahydrate, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$

Uses

Strontium chloride is used to produce strontium metal by electrolysis. It also is used to prepare other strontium salts, as a desensitizer in dentistry, and in pyrotechnics.

Physical Properties

Anhydrous salt is a colorless, cubic, crystalline solid; refractive index 1.650; density 3.052 g/cm³; melts at 875°C; vaporizes at 1,250°C; very slightly soluble in absolute alcohol and acetone; insoluble in liquid ammonia.

The dihydrate exists as transparent leaflets; refractive index 1.594; density 2.672 g/cm³ at 25°C. The hexahydrate is colorless trigonal crystals or white granules; refractive index 1.536; density 1.93 g/cm³; effloresces in air; melts at

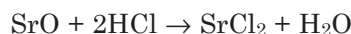
61°C on rapid heating; loses four molecules of water at 115°C; loses all its water at 150°C; highly soluble in water, 106 g/100 mL at 0°C, 206 g/100 mL at 40°C; moderately soluble in alcohol.

Thermochemical Properties

$\Delta H_f^\circ(\text{cry})(\text{SrCl}_2)$	-198.1 kcal/mol
$\Delta H_f^\circ(\text{gas})(\text{SrCl}_2)$	-116.1 kcal/mol
$\Delta H_f^\circ(\text{cry})(\text{SrCl}_2 \cdot 2\text{H}_2\text{O})$	-343.7 kcal/mol
$\Delta H_f^\circ(\text{cry})(\text{SrCl}_2 \cdot 6\text{H}_2\text{O})$	-627.1 kcal/mol
$\Delta G_f^\circ(\text{cry})(\text{SrCl}_2)$	-186.7 kcal/mol
$\Delta G_f^\circ(\text{gas})(\text{SrCl}_2)$	-118.6 kcal/mol
$\Delta G_f^\circ(\text{cry})(\text{SrCl}_2 \cdot 2\text{H}_2\text{O})$	-306.4 kcal/mol
$S^\circ(\text{cry})(\text{SrCl}_2)$	27.4 cal/deg mol
$S^\circ(\text{gas})(\text{SrCl}_2)$	74.3 cal/deg mol
$S^\circ(\text{cry})(\text{SrCl}_2 \cdot 2\text{H}_2\text{O})$	52.0 cal/deg mol
$S^\circ(\text{cry})(\text{SrCl}_2 \cdot 6\text{H}_2\text{O})$	93.4 cal/deg mol
$C_p(\text{cry})$	18.1 cal/deg mol
$C_p(\text{gas})$	13.3 cal/deg mol
$C_p(\text{cry})$	38.3 cal/deg mol

Preparation

Strontium chloride is prepared by reacting strontium oxide, hydroxide, or carbonate in hydrochloric acid:



On evaporation, the solution forms crystals of hydrated chloride which can be dehydrated to anhydrous salt.

Analysis

Elemental composition (for anhydrous SrCl_2): Sr 55.27%, Cl 44.73%. The salt is dissolved in water and analyzed for strontium by various instrumental techniques (see Strontium). Chloride ion is measured by ion chromatography or titration with a standard solution of silver nitrate, using potassium chromate indicator.

STRONTIUM HYDROXIDE

[18480-07-4]

Formula $\text{Sr}(\text{OH})_2$; MW 121.63; forms an octahydrate, $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, MW 265.76

Uses

Strontium hydroxide is used in extracting sugar from beet sugar molasses

and in making lubricant soaps and greases.

Physical Properties

White deliquescent crystal; density 3.625 g/cm³; melts at 375°C in hydrogen atmosphere; converts to oxide at 710°C; slightly soluble in water at 0°C, 0.41 g/100 mL, soluble in boiling water at 100°C, 21.83 g/100 mL; soluble in acids and ammonium chloride solution.

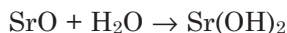
The octahydrate consists of colorless, tetragonal, deliquescent crystals; density 1.90 g/cm³; loses all its water molecules at 100°C; sparingly soluble in water at low temperatures, 0.90 g/100 mL at 0°C; soluble in boiling water, 47.7 g/100 mL at 100°C; aqueous solution highly alkaline; soluble in acids and in ammonium chloride solution; insoluble in acetone.

Thermochemical Properties

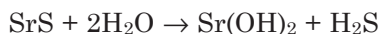
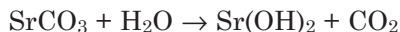
$\Delta H_f^\circ(\text{cry})$	-229.2 kcal/mol
$\Delta H_f^\circ(\text{gas})$	-135.0 kcal/mol

Preparation

Strontium hydroxide is prepared by treating strontium oxide with water:



Alternatively, Sr(OH)₂ is made by heating strontium carbonate or strontium sulfide with steam at temperatures around 500 to 600°C:



Analysis

Elemental composition: Sr 72.03%, O 26.31%, H 1.66%. The aqueous solution may be analyzed to measure strontium content. Basic strength (concentration of the OH⁻) may be determined by acid-base titration.

Toxicity

Dry compound or aqueous solution is corrosive. Contact with skin or eyes can cause irritation.

STRONTIUM NITRATE

[10042-76-9]

Formula Sr(NO₃)₂; MW 211.63; also forms a tetrahydrate Sr(NO₃)₂•4H₂O; MW 283.69

Uses

Strontium nitrate is used in pyrotechnics, for producing marine and rail-

road signals, and in matches.

Physical Properties

Colorless cubic crystals or white powder or granules; density 2.986 g/cm³; melts at 570°C; very soluble in water, 80 g/100 mL at 18°C; very slightly soluble in ethanol.

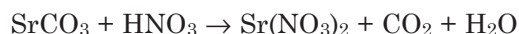
The tetrahydrate constitutes colorless monoclinic crystals; density 2.20 g/cm³; loses all water of crystallization at 100°C; converts to strontium oxide, SrO at 1,100°C; very soluble in water, 60.4g/100 mL at 0°C, 206 g/100 mL at 100°C; soluble in liquid ammonia; very slightly soluble in ethanol and acetone.

Thermochemical Properties

ΔH_f° (cry)	-233.8 kcal/mol
ΔH_f° (aq, 1M)	-229.6 kcal/mol
ΔG_f° (cry)	-186.5 kcal/mol
ΔG_f° (aq, 1M)	-186.9 kcal/mol
S° (cry)	46.5 cal/deg mol
S° (aq, 1M)	62.2 cal/deg mol
C_p (cry)	35.8 cal/deg mol

Preparation

Strontium nitrate is prepared by treating strontium carbonate with nitric acid. The solution is evaporated and crystallized:



Crystallization yields the tetrahydrate, $\text{Sr(NO}_3)_2 \cdot 4\text{H}_2\text{O}$, which on heating dehydrates to form the anhydrous nitrate.

Analysis

Elemental composition: Sr 41.40%, N 13.24%, O 45.36%. An aqueous solution of the salt may be analyzed for strontium by AA, ICP, or other methods. The nitrate anion may be measured by ion chromatography or by nitrate ion-specific electrode.

STRONTIUM OXIDE

[1314-11-0]

Formula SrO; MW 103.62

Synonyms: strontia; strontium monoxide

Uses

Strontium oxide is used for preparing other strontium compounds.

Physical Properties

Grayish-white porous mass; cubic crystalline structure; refractive index

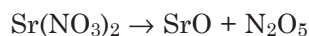
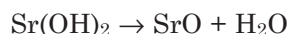
1.810; density 4.70 g/cm³; melts at 2430°C; vaporizes above 3,000°C; reacts with water forming strontium hydroxide, Sr(OH)₂ with evolution of heat; miscible with fused caustic potash; slightly soluble in alcohol; insoluble in acetone and ether.

Thermochemical Properties

ΔH_f°	-141.5 kcal/mol
ΔG_f°	-134.3 kcal/mol
S°	13.0 cal/deg mol
C_p	10.8 cal/deg mol

Preparation

Strontium oxide is prepared by thermal decomposition of strontium carbonate, hydroxide, or nitrate:



Analysis

Elemental composition: Sr 84.56%, O 15.44%. The oxide is digested cautiously in acid, diluted, and analyzed for strontium. The oxide is converted cautiously to hydroxide by treatment with water and the strength of the hydroxide is measured by acid-base titration.

STRONTIUM SULFATE

[7759-02-6]

Formula SrSO₄; MW 183.68

Occurrence and Uses

Strontium sulfate occurs in nature as mineral celestite, which is the principal ore of strontium. The sulfate is the starting material for producing strontium metal and practically all its salts. The sulfate also is used in pyrotechnics and in ceramics.

Physical Properties

White crystalline powder; orthorhombic crystals; refractive index 1.622; hardness 3.3 Mohs; density 3.96 g/cm³; melts at 1,605°C; very slightly soluble in water 0.014 g/100mL at 30°C; soluble in alkali chloride solutions; slightly soluble in alcohol; insoluble in alkalis.

Thermochemical Properties

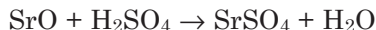
ΔH_f°	-347.3 kcal/mol
ΔG_f°	-320.05 kcal/mol

S°

28 cal/deg mol

Production

Strontium sulfate occurring in nature as celestite is mined from its natural deposits. Also, the sulfate can be made by reacting strontium oxide, hydroxide, or carbonate with dilute hydrochloric acid:

**Analysis**

Elemental composition: Sr 47.70%, S 17.46%, O 34.84%. Strontium sulfate can be characterized by x-ray crystallography. A nitric acid extract is analyzed for strontium. An aqueous solution (the salt is only slightly soluble) is filtered or decanted from insoluble material and measured by ion chromatography.

SULFUR

[7704-34-9]

Symbol S; atomic number 16; atomic weight 32.06; a Group VI A (Group 16) nonmetallic oxygen-group element; electron configuration [Ne]3s²3p⁴; valence states 2, 4, 6; electronegativity 2.5; atomic radius 1.03Å; ionic radius 0.37Å for S⁴⁺ with coordination number 6 and S⁶⁺ having coordination number 4, the hexacoordinated S⁶⁺ in crystals have ionic radius 0.29Å; four naturally-occurring stable isotopes: S-32 (95.02%), S-33 (0.75%), S-34 (4.21%), S-36 (0.02%); thirteen artificial radioactive isotopes in the mass range 27, 29–31, 35, 37–44; the longest-lived radioisotope is the beta-emitter S-35, *t*_{1/2} 87.2 days.

History, Occurrence, and Uses

Sulfur was known to the alchemists from ancient times as brimstone. Lavoisier in 1772 proved sulfur to be an element. The element derived its name from both the Sanskrit and Latin names *Sulvere* and *Sulfurium*, respectively. Sulfur is widely distributed in nature, in earth's crust, ocean, meteorites, the moon, sun, and certain stars. It also is found in volcanic gases, natural gases, petroleum crudes, and hot springs. It is found in practically all plant and animal life. Most natural sulfur is in iron sulfides in the deep earth mantle. The abundance of sulfur in earth's crust is about 350 mg/kg. Its average concentration in seawater is estimated to be about 0.09%. Sulfur occurs in earth's crust as elemental sulfur (often found in the vicinity of volcanoes), sulfides, and sulfates. The most important sulfur-containing ores are iron pyrite, FeS₂; chalcopyrite, CuFeS₂; sphalerite, ZnS; galena, PbS; cinnabar HgS; gypsum CaSO₄•2H₂O; anhydrite CaSO₄; kieserite, MgSO₄•H₂O; celestite, SrSO₄; barite, BaSO₄; and stibnite, Sb₂S₃.

Important sulfur compounds include sulfuric acid, sulfur dioxide, hydrogen

sulfide, sulfur trioxide, and a number of metal sulfides and metal oxo- salts such as sulfates, bisulfates, and sulfites. Numerous organic compounds contain sulfur, such as mercaptans, thiophenes, thiophenols, sulfate esters, sulfones, and carbon disulfide.

Elemental sulfur is used for vulcanizing rubber; making black gunpowder; as a soil conditioner; as a fungicide; preparing a number of metal sulfides; and producing carbon disulfide. It also is used in matches; bleaching wood pulp, straw, silk, and wool; and in synthesis of many dyes. Pharmaceutical grade precipitated and sublimed sulfurs are used as scabicides and as antiseptics in lotions and ointments.

Physical Properties

Sulfur exists in several allotropic forms; at ordinary temperatures it exists as thermodynamically stable alpha-cyclooctasulfur (S_8). The cyclooctasulfur also has two other modifications, the beta and the gamma forms.

Alpha cyclooctasulfur or the alpha-sulfur is yellow orthorhombic crystalline solid; refractive index 1.957; density 2.07 g/cm^3 at 20°C ; stable at ordinary temperatures; converts to monoclinic beta form at 94.5°C .

Beta-sulfur is pale-yellow, opaque needle-like crystals; monoclinic structure; brittle; stable between 94.5 to 120°C ; converts to orthorhombic form on standing; density 1.96 g/cm^3 ; melts at 115.2°C .

Gamma-sulfur is a second monoclinic form of cyclooctasulfur; pale-yellow amorphous solid; density 1.92 g/cm^3 ; melts around 120°C .

There are also various other forms of sulfur including cyclohexa- (S_6), cyclohepta- (S_7), cyclonona- (S_9), cyclodeca- (S_{10}) and cyclododeca (S_{12}) sulfur. Polymeric amorphous sulfur of molecular weight about 200,000 also is known.

Liquid sulfur consists of cyclic S_8 molecules below 159°C . Above this temperature, the cyclic molecules break down forming linear polymers of varying chain lengths. Also, liquid sulfur possibly contains smaller S_6 rings.

Sulfur vapor consists of several small molecules from S_1 through S_4 and cyclic S_5 through S_{10} . At low pressures and temperatures above $1,500^\circ\text{C}$, sulfur occurs in vapor phase in monoclinic S_1 form. At temperatures between approximately 500 to $1,500^\circ\text{C}$ and subatmospheric pressures, the diatomic oxygen-like S_2 form predominates. The S_3 and S_4 molecules of uncertain structures and the S_5 to S_{10} rings are usually minor components of sulfur vapors.

Sulfur vaporizes at 444.6°C . The element, particularly in its orthorhombic S_8 form, is insoluble in water but dissolves in carbon disulfide, anhydrous liquid ammonia, and methylene iodide. It is moderately soluble in benzene, toluene, chloroform, and acetone, solubility increasing with temperature. Solid polymeric sulfur is practically insoluble in all solvents.

Thermochemical Properties

ΔH_f° (orthorhombic)	0.0 kcal/mol
ΔH_f° (monoclinic)	0.08 kcal/mol
ΔH_f° (gas)	66.64 kcal/mol
ΔG_f° (orthorhombic)	0.0 kcal/mol
ΔG_f° (gas)	56.95 kcal/mol

S° (orthorhombic)	7.60 cal/deg mol
S° (gas)	40.08 cal/deg mol
C _p (orthorhombic)	5.41 cal/deg mol
C _p (gas)	5.66 cal/deg mol

Production

Elemental sulfur is recovered from its ore deposits found throughout the world. It is obtained commercially by the Frasch process, recovery from wells sunk into salt domes. Heated water under pressure is forced into the underground deposits to melt sulfur. Liquid sulfur is then brought to the surface. Sulfur is recovered by distillation. Often the ore is concentrated by froth flotation.

Elemental sulfur also is recovered as a by-product in processing natural gas and petroleum. Refining operations of natural gas and petroleum crude produce hydrogen sulfide, which also may occur naturally. Hydrogen sulfide is separated from hydrocarbon gases by absorption in an aqueous solution of alkaline solvent such as monoethanol amine. Hydrogen sulfide is concentrated in this solvent and gas is stripped out and oxidized by air at high temperature in the presence of a catalyst (Claus process).

Elemental sulfur also may be obtained by smelting sulfide ores with a reducing agent, such as coke or natural gas, or by reduction of sulfur dioxide.

Reactions

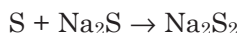
Sulfur forms two oxides, sulfur dioxide, SO₂, and the trioxide, SO₃. It burns in oxygen at about 250°C or in air above 260°C, forming sulfur dioxide. In excess oxygen the trioxide is obtained.

Sulfur reacts with hydrogen at 260 to 350°C forming hydrogen sulfide. The reaction is slow at this temperature and does not go to completion. The reaction is catalyzed by activated alumina.

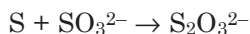
Reactions with excess chlorine or fluorine yield sulfur tetrachloride, SCl₄, or hexafluoride, SF₆. These reactions occur under cold conditions.

Sulfur reacts with sulfur dioxide in an electric discharge to form disulfur dioxide, S₂O.

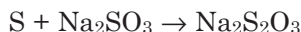
Sulfur reacts with aqueous sulfide to form polysulfides:



With aqueous solution of sulfite the product is thiosulfate:



Thiosulfate also is obtained by heating sulfur with powdered sulfite:



When heated with alkali cyanide, thiocyanate salt is obtained:



A similar reaction occurs in the aqueous phase in which thiocyanate is obtained by evaporation and crystallization.

Sulfur combines with alkali metals, copper, silver, and mercury on cold contact with the solid, forming sulfides. Reactions with magnesium, zinc, and cadmium occur to a small degree at ordinary temperatures, but rapidly on heating. Sulfur reacts with phosphorus, arsenic, antimony, bismuth, and silicon at their melting points and with other elements at elevated temperatures forming binary sulfides. Sulfides of tellurium, gold, platinum, and iridium are difficult to obtain even at elevated temperatures. Sulfur does not react with inert gases, nitrogen, and iodine.

Analysis

Sulfur can be analyzed by x-ray, GC and GC/MS techniques. Alpha-octacyclosulfur is dissolved in benzene, toluene, or chloroform and analyzed for sulfur by GC using a flame photometric detector or by GC/MS. The characteristic mass ions for its identification are multiples of 32 (i.e. 32, 64, 128, and 256). Sulfur may be identified by mixing a little powder with copper, silver, or mercury at room temperature and identifying the metal sulfide from color change and various instrumental methods.

SULFUR CHLORIDE

[10025-67-9]

Formula S_2Cl_2 ; MW 135.04; linear Cl-S-S-Cl chain; S-S bond distance 1.95Å and S-Cl distance 2.05Å

Synonyms: disulfur dichloride; sulfur subchloride; sulfur monochloride

Uses

Sulfur chloride is a solvent for sulfur and a chlorinating agent. Other applications are vulcanizing rubber; an intermediate in making sulfur dyes, synthetic rubber, thionyl chloride, and several other compounds; pesticide formulations; hardening soft woods; and extracting gold.

Physical Properties

Yellowish red oily liquid; pungent penetrating odor; fumes in air; refractive index 1.670 at 20°C; density 1.69 g/mL; dipole moment 1.60; dielectric constant 4.9 at 22°C; freezes at -77°C; boils at 137°C; reacts with water; soluble in ethanol, benzene, ether, chloroform, and carbon tetrachloride; dissolves sulfur at ambient temperature (67 g/100 g sulfur chloride).

Thermochemical Properties

ΔH_f° (liq) -14.2 kcal/mol

Preparation

Sulfur chloride is prepared as an orange liquid by passing chlorine gas through molten sulfur. If excess chlorine is passed and in the presence of a trace FeCl_3 or iodine as catalyst, an equilibrium mixture of about 85% dichloride, SCl_2 , and 15% S_2Cl_2 is obtained. The dichloride dissociates to sulfur chloride:



Sulfur chloride is separated by fractional distillation.

Analysis

Elemental composition: S 47.48%, Cl 52.52%. Sulfur chloride is identified by its physical and chemical properties. It may be analyzed by GC-ECD or GC-FPD. For GC-ECD analysis, a non-chlorine solvent must be employed. The compound can be confirmed from mass spectra obtained from the GC/MS analysis.

Toxicity

Sulfur chloride is toxic and a lachrymator. The vapors can cause irritation of the eyes, nose, and respiratory tract.

SULFUR DIOXIDE

[7446-09-5]

Formula SO_2 ; MW 64.06

Synonyms: sulfurous oxide; sulfurous anhydride

Uses

Sulfur dioxide has a wide range of industrial applications, the most notable being as an intermediate in producing sulfuric acid. It is used to produce chlorine dioxide, sodium bisulfite, and sodium dithionate, which are all bleaching agents. Also, sulfur dioxide itself is a bleaching agent used in bleaching textile fibers, straw, glue, gelatin, and other substances. Sulfur dioxide is used extensively in the food industry to preserve vegetables and dry fruits such as apricots and cherries; as a bleach and steeping agent for grains; to prevent growth of bacteria in processing soy proteins; in refining sugar; as an additive to wine to destroy molds, bacterias, and undesired wild yeast; to prevent formation of nitrosamines in beer in the malting process; and in producing high-fructose corn syrups.

Sulfur dioxide is used in removing oxygen in petroleum recovery processes to prevent corrosion in piping and storage systems. Also, it is applied in water treatment to reduce residual chlorine. In clay processing it reduces iron compounds and other color-forming impurities. Other uses are extracting sulfide ores; casting magnesium; catalyst modifier in certain organic oxidation reac-

tions; and colorimetric analysis of sulfite ion in aqueous samples. In the chemical industry, sulfur dioxide is used as a reducing agent in a number of preparative and analytical reactions. Liquid sulfur dioxide is used as a solvent for sulfur trioxide in sulfonation.

Sulfur dioxide occurs in nature in volcanic gases. It is found in the upper atmosphere at varying but trace concentrations resulting from natural processes and human activities. It occurs in the automotive exhausts and in many fire and stack emission gases. It is produced from burning sulfur-containing fuels, such as coal and oil. Also, it is produced in the petroleum refining process. Sulfur dioxide is partly responsible for causing acid rain.

Physical Properties

Colorless gas; pungent suffocating odor; gas density 2.927 g/L at 20°C; heavier than air, vapor density 2.263 (air=1); condenses to a colorless liquid at -10°C; density of liquid SO₂ 1.434 g/mL; freezes at -72.7°C; critical temperature 157.65°C; critical pressure 77.78 atm; critical volume 122 cc/g; dielectric constant 17.27 at -16.5°C; dissolves in water forming sulfurous acid, solubility 22.97 g and 11.58 g/100mL water at 0° and 20°C, respectively, under atmospheric pressure; very soluble in acetone, methyl isobutyl ketone, acetic acid, and alcohol; soluble in sulfuric acid; liquid SO₂ slightly miscible in water.

Thermochemical Properties

ΔH_f° (gas)	-70.94 kcal/mol
ΔH_f° (liq)	-76.60 kcal/mol
ΔG_f° (gas)	-71.75 kcal/mol
S° (gas)	59.30 cal/deg mol
C_p (gas)	9.53 cal/deg mol
ΔH_{vap}	5.96 kcal/mol

Production

Sulfur dioxide is manufactured mostly by combustion of sulfur or its iron sulfide mineral, pyrite, FeS₂, in air. The flame temperatures for such combustion of sulfur in the air are usually in the range 1,200 to 1,600°C. Many types of sulfur burners are available and are used to produce sulfur dioxide. They include rotary-kiln, spray, spinning-cup and air-atomizing sulfur burners. Selection and design of burners depend on quality of sulfur to be burned, and rate and concentration of sulfur dioxide to be generated. Pyrites or other metal sulfides may be burned in air in fluid-bed roasters to form sulfur dioxide.

Other sources of sulfur dioxide are flue gases and spent sulfuric acid. Sulfur dioxide may be recovered from stack gases in smelting or power plants. Similarly, SO₂ can be generated from spent sulfuric acid recovered from oil refineries. The spent acid is burned in a high temperature furnace above 900°C to form sulfur dioxide, water, and gaseous products.

Liquid sulfur dioxide can be produced by passing a stream of sulfur trioxide, SO₃, through molten sulfur:



Trace sulfur trioxide in the product may be removed by passing the product sulfur dioxide through sulfuric acid.

Reactions

Sulfur dioxide combines with oxygen on heating and in the presence of a catalyst. This reaction proceeds at temperatures between 400 to 700°C with vanadium pentoxide catalyst to make sulfuric acid:



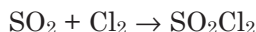
In the upper atmosphere such oxidation of sulfur dioxide to its trioxide forming sulfuric acid or sulfate anion may occur at ambient temperature at a much slower rate in the presence of various free radicals.

Sulfur dioxide dissolves in water forming sulfurous acid that is stable only in solution:

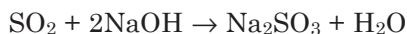


The acid has never been isolated in pure form. It is a weak acid. The $\text{pK}_{\text{a}1}$ and $\text{pK}_{\text{a}2}$ values are 1.85 and 7.20, respectively. When concentrated acid solution is cooled, it crystallizes forming a hexahydrate of sulfur dioxide, $\text{SO}_2 \cdot 6\text{H}_2\text{O}$.

Reactions with chlorine or bromine yield sulfuryl chloride, SO_2Cl_2 , or sulfuryl bromide, SO_2Br_2 :



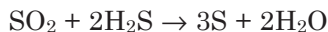
Sulfur dioxide reacts with bases, such as alkali or alkaline-earth oxides and hydroxides to form corresponding metal sulfites and bisulfites:



Such reactions occur with alkalies in solutions, slurries, or solid form. Products and yields depend on temperature and concentrations of reacting bases. At high concentrations and temperatures metabisulfites are produced:

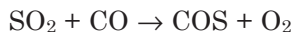
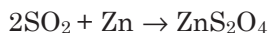
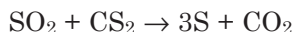
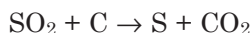
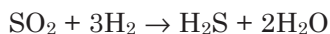


When heated with hydrogen sulfide at 300°C, sulfur dioxide is reduced forming sulfur and water:



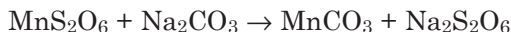
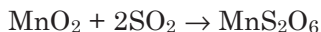
In the presence of moisture or a catalyst, such as silica, or alumina, the reaction can occur at ambient temperature.

Sulfur dioxide also can be reduced by hydrogen, carbon, carbon monoxide, carbon disulfide, certain metals, metal hydrides, and sodium borohydride when heated at high temperatures:

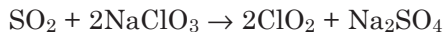


Reduction with carbon monoxide at high temperatures can form either carbonyl sulfide or sulfur depending on the catalyst used. With cobalt molybdate, COS is the primary product. On the other hand, lanthanum titanate catalyzes the reaction to form sulfur.

Sulfur dioxide reacts with manganese dioxide to form manganese dithionate, which is an intermediate in the production of sodium dithionate:



Sulfur dioxide serves as a reducing agent in many preparative reactions. It reduces sodium chlorate in sulfuric acid solution to form chlorine dioxide. The reaction is used to produce chlorine dioxide *in situ*, a bleaching agent in the pulp and paper industry:



Sulfur dioxide reduces hydrogen peroxide to form sulfuric acid:

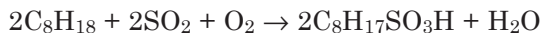


Sulfur dioxide is used as a reducing agent in many organic reactions. It reduces quinones, disulfides, nitroaromatics, and diazo compounds.

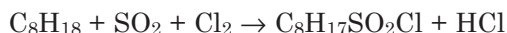
An organic reaction of interest is the Diels-Alder reaction that sulfur dioxide undergoes with butadiene and other acyclic dienes. With butadiene, the product is sulfolene, $\text{C}_4\text{H}_6\text{S}$, a five-membered S-heterocyclic ring compound which is hydrogenated to form sulfolane, $\text{C}_4\text{H}_8\text{S}$.

Sulfur dioxide undergoes sulfoxidation and sulfochlorination with alkanes.

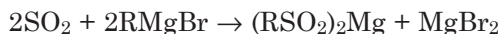
When the gas is simultaneously passed along with oxygen through an alkane in the presence of light, a sulfonic acid forms:



A similar sulfochlorination (or chlorosulfonation) reaction occurs when sulfur dioxide and chlorine are passed simultaneously through the hydrocarbon:



With Grignard reagents, sulfur dioxide reacts to form sulfinic acid salts:



Analysis

Sulfur dioxide may be analysed by GC-FPD, GC-TCD, and GC/MS. The molecular ion for its GC/MS identification is 64. Also, the SO_2 may be measured by colorimetry. It is purged with nitrogen gas and trapped in an absorbing solution containing Fe^{3+} and 1,10-phenanthroline. The Fe^{3+} is reduced to Fe^{2+} forming an orange complex. After removing excess Fe^{3+} with ammonium bifluoride, absorbance of the orange complex is measured at 510 nm.

Toxicity

Sulfur dioxide is highly toxic. It causes severe irritation of eyes, skin, and respiratory tract. Effects are coughing, suffocation, and bronchial constriction.

SULFUR HEXAFLUORIDE

[2551-62-4]

Formula SF_6 ; MW 146.05

Uses

Sulfur hexafluoride is used as a gaseous insulator for electrical equipment and in electronic ultrahigh frequency devices.

Physical Properties

Colorless, odorless gas; density 6.41 g/L; about five times heavier than air; liquefies at -50.7°C (triple point); density of liquid 1.88 g/mL at -50.7°C ; sublimates at -63.8°C ; critical temperature 45.54°C ; critical pressure 37.13 atm; critical volume 199 cm^3/mol ; slightly soluble in water; soluble in ethanol.

Thermochemical Properties

ΔH_f°	-289.0 kcal/mol
ΔG_f°	-264.2 kcal/mol

S°	69.72 cal/deg mol
C_p	23.25 cal/deg mol

Preparation

Sulfur hexachloride may be prepared by reacting fluorine with sulfur or sulfur dioxide.

Analysis

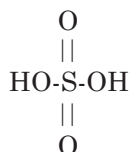
Elemental composition: S 21.95%, F 78.05%. The compound may be identified from its mass spectra. The characteristic mass ions are 146, 127, and 108.

SULFURIC ACID

[7664-93-9]

Formula H_2SO_4 ; MW 98.08

Structure



Synonym: oil of vitriol

The fuming sulfuric acid or oleum, $\text{H}_2\text{SO}_4 \cdot x\text{SO}_3$ [8014-95-7] is a mixture of sulfur trioxide dissolved in sulfuric acid. The SO_3 content may range between 15 and 30%.

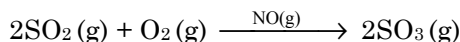
Uses

Sulfuric acid probably is the most important industrial chemical of modern time. In production, it is the largest volume chemical produced in the United States. Most sulfuric acid manufactured in the USA is used by the fertilizer industry for making phosphoric acid and phosphate fertilizers. Sulfuric acid has numerous applications. Some major uses include extracting ores; pickling metal; making explosives; manufacturing dyes, glues, and parchment papers; producing nitric and other acids; purifying petroleum; preparing metal sulfates; and synthesizing many organics. Sulfuric acid also is used in lead storage batteries for automobiles. The lead storage battery was invented by Gaston Plante in 1859. Sulfuric acid is used heavily in sulfonation, esterification, oxidation, dehydration, and acid-base neutralization reactions. Sulfuric acid is a common laboratory reagent used for laboratory preparation of a large number of salts; as a dehydrating agent; as a component of chromic mixture for cleaning glassware; and in acid-base titration. The acid has been in wide usage in various industrial applications for more than two hundred years. Commercial concentrated acid has an assay of 95 to 98% H_2SO_4 . Its normality is 36 N and density 1.834 to 1.836 g/mL.

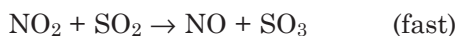
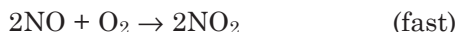
Manufacture

Sulfuric acid is manufactured by two processes; namely, the chamber process and the contact process. The chamber process was discovered in 1746 and was used to produce sulfuric acid for over a century. This process was replaced by the contact process which has a lower production cost and yields a more concentrated acid needed for most industrial applications. The chamber process is obsolete now but for historical interest it is outlined below.

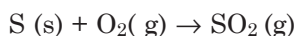
In the chamber process, nitric oxide catalyzes the oxidation of sulfur dioxide to trioxide:



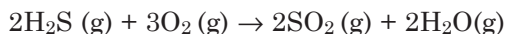
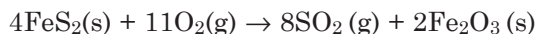
The reaction is homogeneously catalyzed by NO. Although the oxidation process is exothermic and spontaneous, the reaction is very slow without a catalyst. The mechanism of the reaction is as follows:



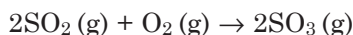
Practically all sulfuric acid is now made by the contact process. The starting material is sulfur dioxide, which is made by various methods, such as burning sulfur in dry air:



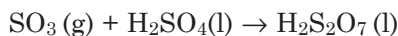
or by burning pyrites or hydrogen sulfide:



Sulfur dioxide produced is reacted with oxygen in the presence of a catalyst to form sulfur trioxide:



Sulfur trioxide produced above by the contact process is absorbed in sulfuric acid to form pyrosulfuric acid, $\text{H}_2\text{S}_2\text{O}_7$, which is diluted with water to form sulfuric acid:



Sulfur trioxide also can be dissolved in water to form sulfuric acid. The dissolution of sulfur trioxide mist, however, is difficult to attain. Most plants

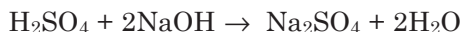
employ sulfuric acid to dissolve SO_3 vapor which can be diluted to obtain sulfuric acid of desired concentration.

Conversion of sulfur dioxide to trioxide requires a suitable catalyst. Vanadium pentoxide, V_2O_5 , is probably the most effective catalyst for the contact process. Vanadium and potassium salts supported on diatomaceous earth, platinized asbestos, platinized magnesium sulfate, and ferric oxide also have proved to be efficient catalysts.

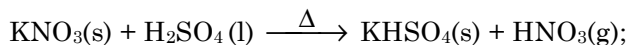
Lead, tantalum, zirconium, and many specialty alloys are not attacked by concentrated acid even at moderate temperatures. Containers made of such materials can be used for handling, storage, and carrying out reactions.

Reactions

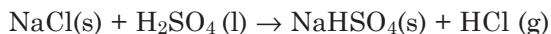
Sulfuric acid is a strong diprotic acid. In dilute aqueous solution, ionization of the first hydrogen is complete and the K_a value for the hydrogen sulfate ion, HSO_4^- at 25°C is 1.2×10^{-2} . It neutralizes bases forming corresponding salts and water. Thus, with caustic soda, sodium sulfate is obtained on evaporation of the solution:



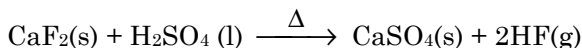
Among some important industrial reactions of sulfuric acid is its reaction with potassium nitrate and distillation of nitric acid from the mixture:



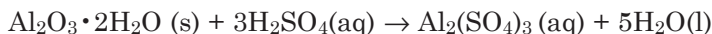
and the production of hydrogen chloride from its reaction with sodium chloride, discovered by Johann Glauber in 1648:



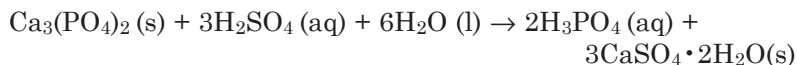
Sulfuric acid reacts with metal halides to form hydrogen halides. Thus, hydrogen fluoride is commercially made by the action of calcium fluoride with the acid:



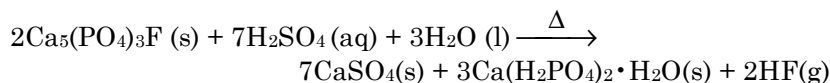
Sulfuric acid reacts with bauxite to yield aluminum sulfate, another important industrial reaction:



Probably the most important commercial reaction of sulfuric acid involves making phosphoric acid from phosphate rock:

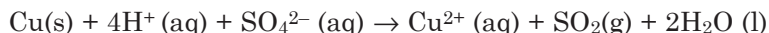


Also, some phosphate rock can be converted directly to super-phosphate fertilizer, which is a mixture of CaSO_4 and $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$:

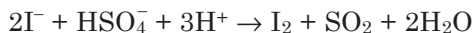


Concentrated acid is a powerful dehydrating agent. It forms hydrates $\text{H}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$. It dehydrates and chars sugar.

In dilute aqueous solution, sulfuric acid is a nonoxidizing acid. However, when concentrated and hot, it is an oxidizing agent. Thus, hot and concentrated sulfuric acid oxidizes copper to Cu^{2+} , liberating sulfur dioxide. The net ionic equation is:



Similar reactions occur with zinc, magnesium, aluminum, and iron. Concentrated sulfuric acid oxidizes iodide to iodine and bromide to bromine:



Sulfuric acid does not manifest such oxidizing action with chloride ion. As mentioned above, reaction with solid sodium chloride forms hydrogen chloride gas, while no such hydrogen halide is produced with corresponding bromide or iodide salt.

Analysis

The normality or molarity of the acid can be determined by titration with a standard solution of sodium hydroxide using a color indicator, or by potentiometric titration using a pH meter or a millivoltmeter. The sulfate anion in dilute acid can be measured by precipitation with barium chloride or by ion chromatography.

Hazard

Sulfuric acid is a highly corrosive acid. Concentrated acid can cause severe burn on skin contact. Contact with eyes can damage vision.

SULFUROUS ACID

[7782-99-2]

Formula H_2SO_3 ; MW 82.08

Sulfurous acid is a solution of sulfur dioxide in water (about 6%). Although it yields sulfite salts, many of which are stable and can be readily prepared, sulfurous acid itself exists in solution only and cannot be isolated in solid crys-

talline form.

The acid is a colorless, clear solution of density about 1.03 g/mL. It emits a suffocating odor of sulfur dioxide and slowly oxidizes in air to sulfuric acid. It is used as an antiseptic and dental bleach solution.

SULFUROUS OXYCHLORIDE

[7719-09-7]

Formula SOCl_2 ; MW 118.97

Synonyms: thionyl chloride; sulfur oxychloride

Uses

Sulfurous oxychloride is used as a chlorinating agent for making sulfoxides and acyl chlorides. It also is used in pesticide formulations and to prepare anhydrous metal halides from their hydrated halides or hydroxides.

Physical Properties

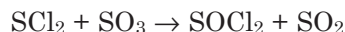
Pale yellow to red fuming liquid; suffocating odor; refractive index 1.517 at 20°C; density 1.631 g/mL at 20°C; freezes at -101°C; boils at 75.6°C; decomposes at 140°C; decomposes in water; soluble in benzene, chloroform, and carbon tetrachloride.

Thermochemical Properties

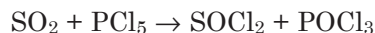
ΔH_f° (liq)	-58.7 kcal/mol
ΔH_f° (gas)	-50.8 kcal/mol
ΔG_f° (gas)	-47.4 kcal/mol
S° (gas)	74.0 cal/deg mol
C_p (liq)	28.9 cal/deg mol
C_p (gas)	15.9 cal/deg mol
ΔH_{vap}	7.58 kcal/mol

Preparation

Sulfurous oxychloride can be prepared by oxidation of sulfur dichloride with sulfur trioxide:

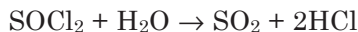


Also, the compound can be prepared by reacting sulfur dioxide with phosphorus pentachloride:



Reactions

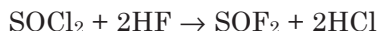
Sulfurous oxychloride is rapidly and violently hydrolyzed in water forming sulfur dioxide and hydrogen chloride:



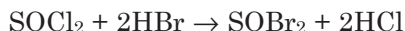
The compound decomposes above 140°C to form sulfur dioxide, chlorine and disulfur dichloride:



Reaction with hydrofluoric acid forms sulfurous oxyfluoride (thionyl fluoride), SOF_2 :



Similar halogen exchange reaction occurs with metal halides. Sulfurous oxybromide is obtained with hydrogen bromide at 0°C:



The compound forms several adducts.

Analysis

Elemental composition: S 26.95%, Cl 59.60%, O 13.45%. The compound may be identified by its physical and chemical properties. A solution in benzene or toluene may be analyzed by GC-ECD or GC-FPD or by the GC/MS, the GC/MS being the most reliable test. For the GC/MS analysis a halogenated solvent such as methylene chloride or chloroform may be used.

Toxicity

Liquid and vapor are highly corrosive to skin and the eye. Vapors are strongly irritating to mucous membranes.

SULFUR TRIOXIDE

[7746-11-9]

Formula SO_3 ; MW 80.064

Synonym: sulfuric anhydride

Uses

Sulfur trioxide is an intermediate in manufacturing sulfuric acid. It is used for sulfonation of organic compounds and in manufacturing explosives.

Physical Properties

Colorless liquid at ambient temperature and atmospheric pressure; fumes in air.

Sulfur trioxide tends to polymerize, particularly in the presence of traces of water or sulfuric acid. The rate of its polymerization, however, decreases

greatly as its freezing point is approached. Solid (polymeric) sulfur trioxide exists in three polymorphic phases: alpha-, beta- and gamma- modifications.

The alpha phase is made up of ice-like needles having polymeric cross-linked structure. It melts at 62.3°C and has a vapor pressure of 73 torr at 25°C.

The beta phase is a metastable allotrope with white, asbestos-like, lustrous needles consisting of polymeric molecules, melting at 32.5°C, and with vapor pressure 344 torr at 25°C.

The gamma modification at ordinary temperatures can exist in solid or liquid form. In solid form it is a colloidal ice-like mass melting at 16.8°C. In the liquid form it has a density of 1.9224 g/mL, boiling at 44.8°C. It has a vapor pressure of 433 torr at 25°C. The gamma phase consists of both cyclic trimer and monomer molecules. When solid sulfur trioxide melts, it converts to its gamma phase which on solidification changes to alpha modification.

Critical temperature of SO_3 is 217.8°C; critical pressure 80.97 atm; critical density 0.63 g/cm³; the dielectric constant of liquid SO_3 at 18°C is 3.11.

Sulfur trioxide dissolves in water forming sulfuric acid and generating large heat.

Thermochemical Properties

ΔH_f° (cry)	-108.63 kcal/mol
ΔH_f° (liq)	-105.41 kcal/mol
ΔH_f° (gas)	-94.58 kcal/mol
ΔG_f° (cry)	-88.19 kcal/mol
ΔG_f° (liq)	-88.04 kcal/mol
ΔG_f° (gas)	-88.69 kcal/mol
S° (cry)	12.50 cal/deg mol
S° (liq)	22.85 cal/deg mol
S° (gas)	61.34 cal/deg mol
C_p (gas)	12.11 cal/deg mol
ΔH_{fus} (alpha)	77.4 kcal/mol
ΔH_{fus} (beta)	36.2 kcal/mol
ΔH_{fus} (gamma)	22.5 kcal/mol

Production

Sulfur trioxide is produced as an intermediate in manufacturing sulfuric acid by the contact process (See Sulfuric Acid). The process involves catalytic oxidation of sulfur dioxide to trioxide.

Sulfur trioxide is prepared in the laboratory by heating fuming sulfuric acid, condensing its vapors, and collecting in a cool receiver. When vapors are condensed below 27°C in the presence of trace moisture, all three polymorphic phases of SO_3 are produced. They can be separated by fractional distillation. Condensation of the vapors above 27°C forms the liquid variety of gamma-sulfur trioxide.

Analysis

Sulfur trioxide is cautiously dissolved in water under cooling to form sulfu-

ric acid. Molarity of the acid is measured by titration with a standard solution of sodium hydroxide. Its vapors may be diluted with helium and analyzed by GC-FPD or GC/MS using a polar column.

Toxicity

Both liquid and vapors are highly corrosive to skin, eyes and mucous membranes.

SULFURYL CHLORIDE

[7791-25-5]

Formula: SO_2Cl_2 ; MW 134.97

Synonyms: sulfonyl chloride; sulfuric chloride; sulfuric oxychloride

Uses

Sulfonyl chloride is used as a chlorinating and sulfonating agent in organic synthesis. It also is used in military gas.

Physical Properties

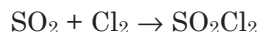
Colorless, mobile liquid; turns yellow on standing; very pungent odor; refractive index 1.4437 at 20°C; density 1.667 g/mL at 20°C; vapors heavier than air, vapor density 4.7 (air=1); melts at -51°C; boils at 69.4°C; sparingly soluble in water, decomposing slowly to sulfuric and hydrochloric acids; forms a hydrate $\text{SO}_2\text{Cl}_2 \cdot 15\text{H}_2\text{O}$ with ice-cold water; miscible with benzene, toluene, chloroform, carbon tetrachloride, and glacial acetic acid; decomposed by alkalis (violent reaction occurs)

Thermochemical Properties

ΔH_f° (liq)	-94.19 kcal/mol
ΔH_f° (gas)	-86.00 kcal/mol
ΔG_f° (gas)	-76.48 kcal/mol
S° (gas)	74.54 cal/deg mol
C_p (liq)	32.03 cal/deg mol
C_p (gas)	18.40 cal/deg mol
ΔH_{vap}	7.50 kcal/mol

Preparation

Sulfonyl chloride is prepared by reacting sulfur dioxide with chlorine in the presence of a catalyst, such as activated carbon or camphor. Both the gases should be in dry form and passed over the catalyst:



Also, the compound can be obtained by heating chlorosulfonic acid in the presence of a catalyst:



Analysis

Elemental composition: S 23.76%, Cl 52.54%, O 23.70%. The compound can be dissolved in an organic solvent, such as toluene, and analyzed by GC using an ECD or FPD type detector or by the GC/MS (a confirmatory analysis). Also, a small amount of compound is decomposed in water (slow reaction) and the products, HCl and H₂SO₄, are measured by ion chromatography or by wet methods

Toxicity

Sulfuryl chloride is highly corrosive to skin, eyes and mucous membranes. Reactions with alkalis, lead dioxide, phosphorus and dimethyl sulfoxide can be violent.

TANTALUM

[7440-25-7]

Symbol Ta; atomic number 73; atomic weight 180.95; a Group VB (Group 5) transition metal in vanadium subgroup; electron configuration [Xe]4f¹⁴5d³6s²; valence state +5; atomic radius 1.46Å; ionic radius of Ta⁵⁺ is 0.64Å for a coordination number 6 in crystals; standard electrode potential, E° for Ta³⁺ + 3e⁻ ↔ Ta is -0.6V; two natural isotopes: Ta-181 (99.988%), Ta-180 (0.012%), Ta-180 is radioactive with a half-life over 1.2x10¹⁵ years; twenty-nine known artificial radioactive isotopes in the mass range 156-179, 182-186.

History, Occurrence and Uses

Tantalum was discovered by the Swedish chemist Anders Ekeberg in 1802, although for a long time after his discovery many chemists believed tantalum and niobium were the same element. In 1866, Marignac developed a fractional crystallization method for separation of tantalum from niobium. Ekeberg named the element in honor of Tantalus, who was Niobe's father in Greek mythology.

Tantalum is never found in nature in free elemental form. The most important mineral is columbite-tantalite (Fe,Mn) (Nb,Ta)₂O₆. Tantalum also is found in minor quantities in minerals pyrochlore, samarskite, euxenite, and fergusonite. The abundance of tantalum in the earth's crust is estimated as 2 mg/kg.

Tantalum and its alloys have high melting points, high strength and ductility and show excellent resistance to chemical attack. Tantalum carbide graphite composite is one of the hardest substances ever made and has a melting point over 6,700°C. The pure metal is ductile and can be drawn into fine wire, which is used as filament for evaporating aluminum and other metals. Tantalum filaments were used in incandescent lamp bulbs before tungsten

replaced them. At temperatures below 150°C, tantalum is attacked only by hydrofluoric acid, fluoride ion in acidic solutions, and free sulfur trioxide. It also is attacked, but slowly, by alkalis. Tantalum and its alloys, therefore, are used to build reactors, vessels, and crucibles for preparing and carrying out reactions involving many reactive intermediates. The metal and its alloys are used to construct furnace parts, electrolytic capacitors, aircraft and missile parts, chemical process equipment, and nuclear reactors. Being nonreactive to body fluids and a nonirritant to body tissues, tantalum is used in making surgical appliances. Plate and sheet tantalum are applied in bone repair, foil and wire for nerve repair, and plate, gauge, and sheet for repair of abdominal muscle. Tantalum oxide is used to produce optical glasses of high refractive index. The oxide film on the metal makes it a rectifier for converting alternating current to direct current.

Physical Properties

Gray, heavy, and very hard metal; malleable and ductile; body-centered cubic lattice structure; the density of the metal 16.65 g/cm³ at 20°C and that of powder 14.40 g/cm³; melts at 2,996°C; vaporizes around 5,458°C; electrical resistivity 13.1 microhm-cm at 25°C; modulus of elasticity 27×10⁶ psi; Poisson's ratio 0.35; magnetic susceptibility 0.849×10⁻⁶ cgs units at 25°C; insoluble in water, alcohol and practically all acids; soluble in hydrofluoric acid

Thermochemical Properties

ΔH_f° (cry)	0.0
ΔH_f° (gas)	186.9 kcal/mol
ΔG_f° (gas)	176.7 kcal/mol
S° (cry)	9.92 cal/deg mol
S° (gas)	44.3 cal/deg mol
C_p (cry)	5.00 cal/deg mol
C_p (gas)	6.91 cal/deg mol
ΔH_{fus}	8.74 kcal/mol
Thermal conductivity (27°C)	0.575 W/cmK
Coefficient of linear expansion (25°C)	6.3×10 ⁻⁶ /°C

Production

Tantalum is mined using techniques such as hydraulic washing and dredging. The ore is crushed, milled, and concentrated by gravity, magnetic, or electrostatic separation or a combination of many wet or dry processes. Ore concentrates consist of tantalum and niobium oxides at varying ratios along with iron, manganese, and small amounts of silica, tin, and titanium. Isolation of tantalum from niobium is usually a tedious and cumbersome process because of their similar chemical properties.

Liquid-liquid extraction is a relatively simple and efficient process compared to Marignac's older fractional crystallization method. Ore concentrate in its finely-ground form is heated with hydrofluoric acid to dissolve the oxides of tantalum and niobium and separate them from associated impurities.

Separation of tantalum from niobium in hydrofluoric acid is carried out by solvent extraction due to solubility difference, using a suitable organic solvent such as methyl isobutyl ketone. At low acidity tantalum partitions from water into immiscible organic solvent leaving behind niobium in the aqueous HF extract. Tantalum is thus separated from this aqueous HF solution. The acidity of the aqueous HF solution is now increased and the solution again extracted with fresh methyl isobutyl ketone to recover niobium, which partitions into the organic solvent, leaving any impurity that may remain dissolved in the HF solution.

The organic extract containing tantalum is treated with pure water upon which tantalum partitions into the aqueous phase as a water-soluble salt.

The aqueous solution on neutralization with ammonia forms tantalum pentoxide, $Ta_2O_5 \cdot nH_2O$. Alternatively, treating the aqueous extract with potassium fluoride yields potassium fluotantalate, K_2TaF_7 .

Marignac's original process has undergone several modifications over the years. Although it has been applied commercially in producing tantalum, the application is very limited. This process can produce tantalum. However, pure niobium cannot be obtained this way. Separation of tantalum from niobium is achieved through fractional crystallization and is based on the solubility difference of potassium fluotantalate, K_2TaF_7 , and potassium pentafluoronio-bate, K_2NbOF_5 , in dilute hydrofluoric acid solution. The tantalate is less soluble than the niobate in dilute HF. In the above process, ore concentrate is fused with caustic soda. The fused mass is treated with hot water and then with hydrochloric acid and filtered. While all impurities are solubilized and remain in the filtrate, the residue essentially consists of hydrated tantalum and niobium oxides. The residue is dissolved in hydrofluoric acid solution and to this solution a potassium salt, usually the hydroxide, fluoride, or carbonate is added. Upon cooling, potassium fluotantalate precipitates from solution.

Tantalum metal is prepared from potassium fluotantalate or tantalum pentoxide produced from the ore concentrate by solvent extraction or fractional crystallization as described. The metal is produced industrially by Balkes electrolysis process. Fused potassium fluotantalate is electrolyzed at $900^\circ C$ in a cast iron pot. While the latter serves as a cathode, a graphite rod is used as the anode. A small amount of tantalum oxide is added to the melt. The unreduced potassium fluotantalate is separated from the tantalum metal produced by leaching with water. Impurities are removed from the metal by acid wash.

Another electrolysis process involves electrodeposition of dense, high-purity tantalum metal. In this electrolysis, electrolyte consists of potassium fluotantalate and potassium fluoride and the anode is made of tantalum upon which electrodeposition from the fused salt occurs.

Thermal reduction processes have been applied successfully in making the metal from salts. In one such process, potassium fluotantalate is reduced with sodium metal at high temperatures to form tantalum powder of high purity and small particle size. Also, tantalum oxide can be reduced at high temperatures in vacuum with aluminum, silicon, or tantalum carbide. When the oxide is reduced by tantalum carbide, a metal sponge is obtained which can be embrittled with hydrogen to form powder metal.

Reactions

The most common oxidation state of tantalum is +5 and its aqueous solution chemistry is that of its pentavalent ion Ta^{5+} . Ta metal forms a pentavalent oxide, tantalum pentoxide, Ta_2O_5 , on heating with oxygen. However, at ordinary temperatures a thin layer of oxide covering the metal surface protects tantalum from most chemical attacks. The metal is attacked by hydrofluoric acid below 150°C. It also is dissolved by hot fuming sulfuric acid. It reacts with fluorine and chlorine on heating, forming tantalum pentafluoride, TaF_5 , and pentachloride, $TaCl_5$, respectively. The metal is immune to dilute aqueous alkalis but is attacked slowly by concentrated fused alkalis. It combines with molecular hydrogen above 250°C. The hydride formed decomposes on heating above 800°C in vacuum. Tantalum forms alloys with several metals.

Analysis

Tantalum may be digested with a mixture of hydrofluoric acid and nitric acid, the solution diluted, and analyzed by flame AA or ICP-AES. Also, tantalum can be identified by x-ray methods and neutron activation analysis.

TANTALUM PENTACHLORIDE

[7721-01-9]

Formula: $TaCl_5$; MW 358.21; shows a dinuclear structure, Ta_2Cl_{10} , but in vapor phase it exists as a mononuclear, $TaCl_5$, having a trigonal bipyramidal shape.

Synonyms: tantalum chloride; tantalic chloride

Uses

Tantalum pentachloride is used to make pure metal and other tantalum salts. Also, it is used for chlorination of organic substances.

Physical Properties

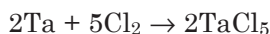
Yellow monoclinic crystals; hygroscopic; density 3.68 g/cm³; melts at 216°C; vaporizes at 239.4°C; critical temperature 494°C; critical volume 402 cm³/mol; can be sublimed without decomposition in chlorine atmosphere; reacts with water; soluble in ethanol, ether and carbon tetrachloride.

Thermochemical Properties

ΔH_f°	-205.3 kcal/mol
ΔH_{fus}	8.39 kcal/mol
ΔH_{vap}	13.1 kcal/mol

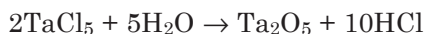
Preparation

Tantalum pentachloride is prepared by heating tantalum metal with excess chlorine:

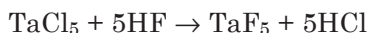


Reactions

Tantalum pentachloride is hydrolyzed by water to form hydrous tantalum pentoxide, $\text{Ta}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ and hydrochloric acid:



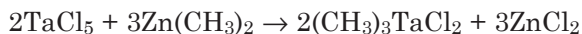
Reaction with hydrofluoric acid yields tantalum pentafluoride:



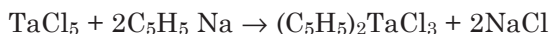
Tantalum pentachloride forms adducts with donor solvent molecules. Also, it forms several complexes and organometallic derivatives.

Reactions with alcohols in the presence of an amine forms dinuclear alkoxides. Thus, with ethanol in the presence of diethylamine, the dinuclear tantalum ethoxide, $\text{Ta}_2(\text{OC}_2\text{H}_5)_{10}$, is obtained.

Reaction with dimethylzinc forms dichlorotrimethyl tantalum, in which three chlorine atoms are substituted with methyl groups:



Reaction with cyclopentadienyl sodium yields bis(cyclopentadienyl) tantalum trichloride:

**Analysis**

Elemental composition: Ta 50.50%, Cl 49.50%. Tantalum content in an acid extract (HF-HNO_3 extract) can be determined by various instrumental techniques. The pentachloride is hydrolyzed to HCl, which can be measured by acid-base titration. Also, the compound can be identified from its physical and x-ray properties.

TANTALUM PENTOXIDE

[1314-61-0]

Formula Ta_2O_5 ; MW 441.89

Synonyms: tantalum oxide; tantalic acid anhydride

Uses

Tantalum pentoxide is used in making high refractive index optical glass; as a dielectric film on tantalum for its use as a capacitor component and rectifier; and for preparing tantalum metal, its carbide, and many other tantalum compounds.

Physical Properties

White orthorhombic crystal or powder; density 8.20 g/cm³; melts at

1,785°C; insoluble in water, ethanol and practically all acids; soluble in hydrofluoric acid; solubilized by fusion with caustic potash or potassium hydrogen sulfate.

Thermochemical Properties

ΔH_f°	-489.0 kcal/mol
ΔG_f°	-456.8 kcal/mol
S°	34.2 cal/deg mol
C_p	32.3 cal/deg mol
ΔH_{fus}	28.7 kcal/mol

Preparation

Tantalum pentoxide is obtained as an intermediate in extracting tantalum from the columbite-tantalite series of minerals. Also, the oxide can be made by heating Ta metal in oxygen or air at elevated temperatures.

Analysis

Elemental composition: Ta 81.89%, O 18.11%. The oxide may be identified by x-ray methods. It may be dissolved in hydrofluoric and nitric acid, diluted and analyzed by AA, ICP and other instrumental techniques.

TECHNETIUM

[7440-26-8]

Symbol Tc; atomic number 43; atomic weight 98; a Group VIIB (Group 7) manganese group metallic element; the first artificially-produced radioactive element; electron configuration $[\text{Kr}]4d^5 5s^2$; valence states 0, +2, +4, +5, +6, +7; most stable oxidation state +7; atomic radius 1.36Å; all isotopes are radioactive; twenty-eight artificially produced isotopes are known in the mass range 86–113; three have long half-lives; Tc-97, $t_{1/2}$ 2.6×10^6 year; Tc-98, $t_{1/2}$ 4.2×10^6 year; and Tc-99, $t_{1/2}$ 2.13×10^5 year.

History, Occurrence and Uses

Existence of technetium was predicted from the vacant position in the Periodic Table between manganese and rhenium. Noddack, Tacke, and Berg reported its discovery in 1925 and named it "masurium." The metal actually was never isolated from any source by these workers. Its existence, therefore, could not be confirmed. Perrier and Segre in 1937 produced this element by bombarding molybdenum metal with deuterons in a cyclotron. They named the element technetium derived from the Greek word *technetos*, meaning artificial.

Technetium has not been found to exist on earth. However, it has been detected in certain stars. Long-lived technetium-99 isotope of half-life 2.15×10^5 years is found in relatively significant quantities in fission products of uranium-235. Every 1g of uranium-235 yields about 0.027g of technetium-99 from its fission.

Technetium metal does not have much commercial application. Its short-

lived metastable isotopes Tc-99m with a half-life of 6 hours is used to locate tumors in liver, brain, spleen, and thyroid by scintillation scanning. It also is used in research. Tc is an excellent corrosion inhibitor for steel and can be used to protect steel. The steel may be confined to a closed system and to prevent any exposure to radiation. This property, however, has not yet been utilized in commercial practice. Also, technetium and its alloys exhibit excellent superconducting properties. They can be used to produce magnetic fields at a low temperature.

Physical Properties

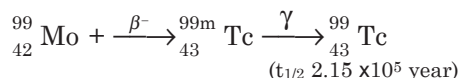
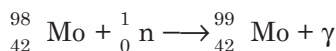
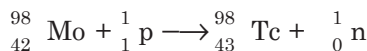
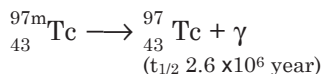
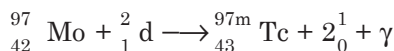
Silvery-gray metal; slowly tarnishes in moist air; crystallizes in hexagonal close-packed structure; density 11.49 g/cm³ (calculated); melts at 2,172°C; vaporizes at 4,265°C; Young's (elastic) modulus 3.76×10^6 kg/cm; Poisson's ratio 0.293; thermal neutron absorption cross-section 22 barns; superconductor below 11°K; insoluble in water and hydrochloric acid; dissolves in nitric acid, concentrated sulfuric acid and aqua regia.

Thermochemical Properties

ΔH_f° (cry)	0.0
ΔH_f° (gas)	162.0 kcal/mol
ΔG_f° (cry)	0.0
S° (gas)	43.25 cal/deg mol
C_p (cry)	4.97 cal/deg mol
ΔH_{fus}	7.96 kcal/mol
Thermal conductivity	0.506 W/cm K
Coefficient of linear expansion	$8.06 \times 10^{-6} / ^\circ\text{C}$

Preparation

Technetium isotopes are prepared by bombardment of molybdenum with protons and neutrons. A few nuclear reactions are shown for the three long-lived isotopes:



Technetium-99 also is a fission product of uranium-235.

Pure technetium metal may be prepared by reducing ammonium pertechnetate, NH_4TcO_4 , with hydrogen at high temperatures. Hydrogen reduction at about 200°C first forms the oxide, TcO_2 , which is reduced to Tc metal at 600 to 800°C .

Reactions

Most chemical properties of technetium are similar to those of rhenium. The metal exhibits several oxidation states, the most stable being the heptavalent, Tc^{7+} . The metal forms two oxides: the black dioxide TcO_2 and the heptoxide Tc_2O_7 . At ambient temperature in the presence of moisture, a thin layer of dioxide, TcO_2 , covers the metal surface. The metal burns in fluorine to form two fluorides, the penta- and hexafluorides, TcF_5 and TcF_6 . Binary compounds also are obtained with other nonmetallic elements. It combines with sulfur and carbon at high temperatures forming technetium disulfide and carbide, TcS_2 and TcC , respectively.

Technetium dissolves in dilute or concentrated nitric acid to form nitrate, $\text{Tc}(\text{NO}_3)_2$. Reaction with concentrated sulfuric acid yields the sulfate TcSO_4 . Technetium is oxidized by hydrogen peroxide in alkaline solution to form soluble pertechnetate, TcO_4^- anion. Such pertechnatate anion forms complexes with tertiary or quarternary amines, pyridine and its methyl-substituted derivatives.

Analysis

Technetium can be measured by spectrophotometric methods. It forms two characteristic peaks with absorption maxima at 247 and 285 nm. Also, it can be measured by polarographic methods. All technetium isotopes are radioactive. The element can be identified from its specific activity using a scintillation counter.

TELLURIC ACID

[7803-68-1]

Formula: H_6TeO_6 or $\text{Te}(\text{OH})_6$; MW 229.64; hydrogen-bonded octahedral molecules

Synonyms: orthotelluric acid; telluric (VI) acid; hydrogen tellurate

Uses

No commercial application of this compound is known. It is used in preparing certain tellurium complexes and tellurates.

Physical Properties

White crystals; dimorphic solid; exists in both cubic and monoclinic crystalline forms; density 3.07g/cm^3 ; melts at 136°C ; tends to polymerize (similar to stannic acid); forms polymetatelluric acid $(\text{H}_2\text{TeO}_4)_n$ on strong heating; sol-

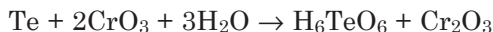
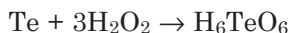
uble in water, about 33g/100 mL at 30°C; the solubility decreases as the molecule polymerizes and becomes colloidal; a very weak dibasic acid, pK_{a1} 7.68 and pK_{a2} 11.0 at 18°C; soluble in dilute nitric acid and alkalies.

Preparation

Telluric acid can be prepared by reducing barium tellurate with sulfuric acid:



Also, telluric acid can be prepared by oxidation of tellurium or tellurium dioxide with a strong oxidizing agent such as hydrogen peroxide, sodium peroxide, chromic acid, or potassium permanganate in nitric acid. Molecular equations for overall reactions are shown below:



At cold temperatures at about 1°C, telluric acid crystallizes as tetrahydrate.

Analysis

Elemental composition: Te 55.57%, H 2.63%, O 41.80%. An aqueous solution or a dilute nitric acid solution is analyzed for tellurium by AA or ICP techniques. Aqueous solution also may be analyzed by colorimetric methods (See Tellurium below).

TELLURIUM

[13494-80-9]

Symbol Te; atomic number 52; atomic weight 127.60; a Group VI A (Group 16) metallic element in the oxygen group placed between selenium and polonium; electron configuration $[\text{Kr}]4d^{10}5s^25p^4$; valence states +2, +4, +6; atomic radius 1.42 Å; ionic radii of Te^{+4} and Te^{+6} in crystals, 0.97 Å and 0.56 Å, respectively, for coordination number 6; electronegativity 2.1; eight naturally-occurring isotopes: Te-120 (0.096%), Te-122 (2.603%), Te-123 (0.908%), Te-124 (18.952%), Te-125 (7.139%), Te-126 (18.952%), Te-128 (31.687%), Te-130 (33.799%); two of these naturally-occurring isotopes are radioactive with very long half-lives, Te-130 ($t_{1/2}$ 2.5×10^{21} year) and Te-123 ($t_{1/2}$ 1.3×10^{13} year); twenty-five artificial radioactive isotopes in the mass range 106–119, 121, 127, 129, 131–138.

History, Occurrence, and Uses

The element was discovered by Muller von Reichenstein in 1782 while investigating a bluish-white ore of gold. The element was isolated from this ore by Klaproth in 1798, who suggested the name “tellurium” after the Latin word *tellus*, meaning earth. Tellurium occurs in nature only in minute quantities. It is found in small amounts in many sulfide deposits. One of the more common tellurium minerals is calaverite, AuTe_2 , in which the metal is combined with gold. Some other tellurium minerals are altaite, PbTe ; sylvanite, $(\text{Ag,Au})\text{Te}_2$; rickardite, Cu_4Te_3 ; tetradymite, $\text{Bi}_2\text{Te}_2\text{S}$; petzite, Ag_3AuTe_2 and coloradoite, HgTe . The metal is found in the native state and also in the form of its dioxide, tellurite, TeO_2 . The abundance of tellurium in the earth's crust is estimated to be about 1 $\mu\text{g/kg}$.

Small amounts of tellurium are added to stainless steel and copper to improve their machinability. It enhances the strength and hardness of lead and protects lead from the corrosive action of sulfuric acid. Tellurium also is a strong chilling agent in iron castings. It controls the chill and imparts a tough abrasion resistance to the surface. Tellurium is a curing agent for natural and synthetic rubber. It improves mechanical properties of the rubber imparting resistance to heat and abrasion. Tellurium is a coloring agent in glass, ceramics, and enamels. Traces of tellurium incorporated into platinum catalysts make the catalytic hydrogenation of nitric oxide favorable to forming hydroxylamine.

A major application of tellurium is in semiconductor research. Tellurides of lead and bismuth are used in thermoelectric devices for power generation and refrigeration.

Physical Properties

Silvery-white lustrous metal when pure or dark gray amorphous powder; orthorhombic crystals; hardness 2.3 Mohs; density 6.25 g/cm^3 ; melts at 452°C; vaporizes at 990°C; modulus of elasticity 6.0 $\times 10^6$ psi; thermal neutron absorption cross section 4.7 $\pm$ 0.1 barns; insoluble in water, carbon disulfide, and benzene; also insoluble in HCl; soluble in sulfuric acid, nitric acid, and aqua regia; also soluble in caustic potash and in solutions of alkali metal cyanides.

Thermochemical Properties

ΔH_f° (cry)	0.0
ΔH_f° (gas)	47.02 kcal/mol
ΔG_f° (cry)	0.0
ΔG_f° (gas)	37.55 kcal/mol
S° (cry)	11.88 cal/deg mol
S° (gas)	43.65 cal/deg mol
C_p (cry)	6.15 cal/deg mol
C_p (gas)	4.97 cal/deg mol
ΔH_{fus}	4.18 kcal/mol
ΔH_{vap}	27.0 kcal/mol
Coefficient of linear expansion	16.75 $\times 10^{-6}/^\circ\text{C}$
ΔH_{vap}	27.3 kcal/mol

Production

Tellurium is recovered from the anode slimes produced in electrolytic refining of copper. Other metals present in these slimes are gold, silver, and selenium, which are all recovered as by-products in the extraction of tellurium. Tellurium is leached with caustic soda solution and the leachate upon neutralization precipitates tellurium dioxide, TeO_2 , in crude and impure form. A part of tellurium remaining in the slimes can be recovered during extraction of gold and silver. In this gold and silver recovery process, tellurium incorporates into the soda slag obtained from roasting the slimes in a furnace. Soda slag is produced when leached with a solution of caustic soda. The liquor is neutralized to form a crude precipitate of tellurium dioxide.

Crude tellurium dioxide is dissolved in a strong solution of caustic soda to form sodium tellurite. Electrolysis of sodium tellurite solution deposits tellurium metal on the stainless steel cathode.

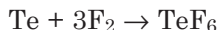
Also, the tellurium metal can be prepared by thermal reduction of dioxide. However, prior to reduction crude dioxide is refined by successive caustic leaching and neutralization steps mentioned above.

Refined tellurium contains traces of lead, copper, iron, selenium, and other impurities. Highly pure tellurium can be obtained either by distilling refined tellurium in vacuum or by the zone melting process. The last traces of selenium can be removed as hydride by treating molten tellurium with hydrogen.

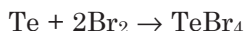
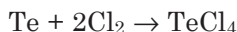
Reactions

Tellurium burns in air with a greenish-blue flame. The combustion product is dioxide, TeO_2 , the most stable oxide of the metal. Tellurium also forms other oxides; the monoxide, TeO , the trioxide, TeO_3 , and the pentoxide, Te_2O_5 . Monoxide has not yet been obtained in solid form. Like sulfur and selenium, tellurium forms oxyacids. Such oxyacids include orthotelluric acid, H_6TeO_6 and tellurous acid, H_2TeO_3 , in which the metal is in +6 and +4 valence states respectively.

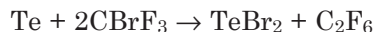
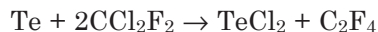
Tellurium combines with halogens forming halides at different oxidation states. While with fluorine, direct fluorination of the metal produces tellurium hexafluoride, TeF_6 , a colorless gas with a repulsive odor:



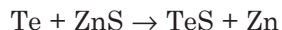
With chlorine and bromine, products are tellurium tetrachloride, TeCl_4 , a white, very hygroscopic crystalline solid, and tellurium tetrabromide, TeBr_4 , an orange crystalline solid:



Tellurium also forms a black dichloride and a brown dibromide usually by its reaction with dichlorodifluoromethane and trifluorobromomethane, respectively:



Tellurium forms many sulfides and oxysulfides. The metal reacts with sulfides of zinc, cadmium, or mercury, forming tellurium sulfide:



The higher sulfides of tellurium such as TeS_2 and TeS_3 , are obtained from tellurite solutions by precipitation with hydrogen sulfide or sodium sulfide. Tellurium reacts with concentrated sulfuric acid to form red oxysulfide of the composition, TeSO_3 . With nitric acid, the metal is oxidized to dioxide, TeO_2 . Oxidation of tellurium with chromic acid or potassium permanganate in nitric acid yields orthotelluric acid (H_6TeO_6).

Tellurium forms binary tellurides with several metals. The reaction is carried out by heating tellurium with a metal in stoichiometric amounts in the absence of air in an evacuated ampoule. Tellurium reacts with halides of several metals, when heated in a stream of hydrogen, to produce metal tellurides.

Analysis

Tellurium and its compounds can be analysed by AA, ICP-AES and other spectrophotometric methods. Also, the metal can be identified by volumetric, gravimetric, and simple colorimetric measurements.

Tellurium metal, its alloys, minerals or the tellurides may be dissolved in warm concentrated sulfuric acid or cold fuming sulfuric acid to form a red color, the intensity of which is proportional to the tellurium content in the substance. When this red solution is poured into water, black elemental tellurium metal precipitates out of solution. Oxidized tellurium does not respond to this test.

An acidic solution of tellurium (IV) or tellurium (VI) is treated with sulfur dioxide and hydrazine hydrochloride. Tellurium precipitated from solution can be estimated by gravimetry. Selenium interferes with this test. A volumetric test involves converting tellurium to tellurous acid and oxidizing the acid with excess ceric sulfate in hot sulfuric acid in the presence of Cr^{3+} ion as catalyst. The excess ceric sulfate is measured by titration with a standard solution of ferrous ammonium sulfate.

Tellurium can be measured by neutron activation analysis.

Toxicity

Human exposure to tellurium causes "garlic breath" due to dimethyl telluride which persists for a considerable period after exposure. The toxic effects of tellurium are nausea, giddiness, headache, metallic taste, and dryness in the throat.